

Lanthanide Picrate Complexes and Picric Acid Adduct of a Calix[4]arene Diamide. Syntheses and Structures of $[\text{Tm}(\text{LH}_{-2})\text{A}]$, $[\text{Ce}(\text{LH}_{-2})(\text{MeOH})_2\text{A}] \cdot \text{HA}$, $[\text{PrLA}_3]$ and $\text{L} \cdot 2\text{HA}$ $\{\text{L} = 5,11,17,23\text{-tetra-}t\text{-butyl-25,27-bis}(\text{diethylcarbamoyl-methoxy})\text{-26,28-dihydroxycalix[4]arene}$, $\text{HA} = \text{picric acid}\}$ †

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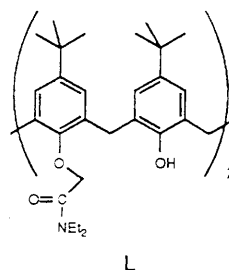
Reactions of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-dihydroxycalix[4]arene (L) with lanthanide picrates produced 1:1 metal-calixarene complexes incorporating one, two or three picrate moieties, depending on the reaction conditions and the lanthanide used. Dichloromethane solutions of L have been found to extract picric acid (HA) from aqueous solution, resulting in the formation of an L·2HA adduct. Single crystal structure determinations have been carried out on $[\text{Tm}(\text{LH}_{-2})\text{A}] \cdot 2.5\text{CH}_2\text{Cl}_2$, $[\text{Ce}(\text{LH}_{-2})(\text{MeOH})_2\text{A}] \cdot \text{HA} \cdot \text{H}_2\text{O}$, $[\text{PrLA}_3] \cdot 2\text{CH}_2\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$ and $\text{L} \cdot 2\text{HA} \cdot \text{EtOH}$. The possible variations of these formulae, depending on the charge distribution within the complexes, are discussed. The calixarene is found in a distorted cone conformation in each case. The intense colour of some of these complexes appears to correlate with the disposition of a picrate moiety close to a calixarene phenyl ring, consistent with calixarene→picrate charge-transfer absorption. The UV/VIS spectroscopic studies suggest that at least some aspects of the solid-state structures are maintained in solution.

Calixarenes are a family of synthetic macrocyclic receptors consisting of cyclic arrays of phenol moieties linked by methylene groups.¹ They can be modified at the lower rim to produce a wide variety of ionophores.² The majority of these receptor molecules incorporate extra oxygen-donor atoms, producing ionophores known to bind alkali-, alkaline-earth-metal and lanthanide cations.^{3–5} Many of these calixarene derivatives feature ionisable phenol or carboxylate groups, so that the stabilities of the complexes formed increase with increasing pH. It has been found, at least for the calixarene acids, that the negatively charged calixarenes favour binding of the lanthanide cations, over alkali- and alkaline-earth-metal cations.⁴ Such lanthanide complexes have been found to exhibit strong fluorescence,^{6–8} which may make them useful as luminescent probes in biological systems, for example.

Despite this activity, there is a paucity of structural data for the complexes of calixarenes in varying protonation states, and on lanthanide-calixarene complexes in general, beyond those of the parent *p-tert*-butylcalixarenes.^{9–14} Investigation of the structure of such complexes should provide information relevant to the design of selective receptors, such as the influence of negative charge on the calixarene, and the effect of small changes in the cation size. We report here the synthesis and structure of lanthanide picrate complexes of the calix[4]arene diamide (L) in protonated and deprotonated forms, as well as a picric acid (HA) adduct of L.

Experimental

Syntheses. — 5,11,17,23-Tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-dihydroxycalix[4]arene¹⁵ (L), and the lanthanide picrate dodecahydrates¹⁶ were synthesised by literature methods.



$[\text{LnLA}_3]$ (Ln = La, Ce, Pr or Eu). A solution of $[\text{LnA}_3] \cdot 12\text{H}_2\text{O}$ (0.025 mmol) in ethanol (1.5 cm³) was added to a solution of the calixarene L (0.023 mmol) in dichloromethane (1.5 cm³). The resulting mixture was filtered and on standing, an orange microcrystalline solid deposited. The product was filtered off, washed with ethanol (2 × 1 cm³) and dried *in vacuo*. The praseodymium and europium complexes were further purified by recrystallisation from dichloromethane-methanol (1:1, 1.5 cm³), giving for the Pr complex, crystals suitable for X-ray diffraction studies (yield, 70–80%). $[\text{LaLA}_3]$ (Found: C, 52.8; H, 5.00; N, 9.35. Calc. for $\text{C}_{74}\text{H}_{84}\text{LaN}_{11}\text{O}_{27}$: C, 52.3; H, 4.50; N, 9.05%). $[\text{CeLA}_3] \cdot \text{H}_2\text{O}$ (Found: C, 51.9; H, 5.20; N, 8.65. Calc. for $\text{C}_{74}\text{H}_{86}\text{CeN}_{11}\text{O}_{28}$: C, 51.7; H, 5.05; N, 8.95%). $[\text{PrLA}_3] \cdot \text{H}_2\text{O}$ (Found: C, 51.6; H, 4.75; N, 9.05. Calc. for $\text{C}_{74}\text{H}_{86}\text{N}_{11}\text{O}_{28}\text{Pr}$: C, 51.7; H, 5.04; N, 8.95%). $[\text{EuLA}_3]$ (Found: C, 51.5; H, 4.90; N, 9.10. Calc. for $\text{C}_{74}\text{H}_{84}\text{EuN}_{11}\text{O}_{27}$: C, 51.4; H, 5.00; N, 8.90%).

$[\text{Ln}(\text{LH}_{-2})(\text{MeOH})_2\text{A}] \cdot \text{HA}$ (Ln = La or Ce). The compound $[\text{LnLA}_3]$ was dissolved in dichloromethane-methanol (1:1, 1.5 cm³). Upon slow evaporation of the dichloromethane, the solution turned dark brown, and large dark brown crystals were slowly deposited. For X-ray diffraction studies, crystals were kept wet with supernatant solution. Crystals collected in the laboratory atmosphere, washed with methanol (2 × 1 cm³) and air dried became opaque. Microanalyses were consistent

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Crystal data and structure refinement for complexes 1–4

	1	2	3	4
Empirical formula	C _{64.5} H ₈₃ Cl ₅ N ₅ O ₁₃ Tm	C ₇₀ H ₉₁ CeN ₈ O ₂₃	C ₇₆ H ₉₁ Cl ₄ N ₁₁ O _{28.5} Pr	C ₇₀ H ₉₀ N ₈ O ₂₁
<i>M</i>	1482.59	1552.66	1897.34	1379.53
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)
λ (Mo-K α)/Å	0.710 70	0.710 70	0.710 70	0.710 70
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	14.100(8)	10.634(8)	12.456(7)	16.221(8)
<i>b</i> /Å	15.136(9)	13.366(8)	13.395(7)	13.188(8)
<i>c</i> /Å	18.201(10)	28.031(9)	27.197(7)	16.856(8)
α /°	88.08(1)	89.33(1)	78.85(1)	
β /°	81.11(1)	81.52(1)	89.55(1)	90.30(1)
γ /°	72.10(1)	78.23(1)	83.86(1)	
<i>U</i> /Å ³	3651(3)	3857(3)	4426(4)	3605(3)
<i>Z</i>	2	2	2	4
<i>D_c</i> /Mg m ^{−3}	1.349	1.337	1.424	1.271
μ /mm ^{−1}	1.457	0.667	0.695	0.094
<i>F</i> (000)	1526	1618	1958	1468
Crystal size/mm	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.4	0.3 × 0.25 × 0.3	0.35 × 0.40 × 0.25
θ range/°	1.74–24.73	2.76–25.04	2.40–25.06	2.51–22.28
Index ranges	0 ≤ <i>h</i> ≤ 16, −16 ≤ <i>k</i> ≤ 17, −20 ≤ <i>l</i> ≤ 21	0 ≤ <i>h</i> ≤ 12, −13 ≤ <i>k</i> ≤ 14, −32 ≤ <i>l</i> ≤ 33	0 ≤ <i>h</i> ≤ 14, −13 ≤ <i>k</i> ≤ 13, −32 ≤ <i>l</i> ≤ 32	−17 ≤ <i>h</i> ≤ 17, 0 ≤ <i>k</i> ≤ 13, −17 ≤ <i>l</i> ≤ 17
Reflections collected	10 295	10 341	11 824	8122
Independent reflections	10 295	10 341	11 824	4355 [<i>R</i> (int) = 0.0357]
No. of data, parameters	10 295, 813	10 341, 933	11 824, 991	4355, 451
Goodness-of-fit on <i>F</i> ²	0.925	0.949	1.069	0.954
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] (<i>R</i> 1, <i>wR</i> 2)	0.0657, 0.1758	0.1073, 0.2965	0.1235, 0.2465	0.0922, 0.2264
<i>R</i> indices (all data) (<i>R</i> 1, <i>wR</i> 2)	0.0897, 0.2321	0.1453, 0.3238	0.1991, 0.3561	0.1464, 0.3528
Largest difference peak, hole/e Å ^{−3}	1.530, −2.067	1.023, −1.278	2.205, −1.631	0.552, −0.405

with loss of solvent relative to the stoichiometries implied by the structure determinations (yield, 85%). [La(LH₂)(MeOH)A]·HA (Found: C, 55.3; H, 5.50; N, 7.60. Calc. for C₆₉H₈₅LaN₈O₂₁: C, 55.2; H, 5.70; N, 7.45%). [Ce(LH₂)(MeOH)A]·HA (Found: C, 55.3; H, 5.50; N, 7.55. Calc. for C₆₉H₈₅CeN₈O₂₁: C, 55.1; H, 5.70; N, 7.45%).

[Tm(LH₂)A]. A solution of [Tm(A₃)]·12H₂O (0.025 mmol) in ethanol (1.5 cm³) was added to a solution of the calixarene L (0.023 mmol) in dichloromethane (1.5 cm³). Triethylamine (0.02 cm³) was then added, to give a dark brown solution, which was filtered and left to evaporate. The product precipitated as large dark brown rhombs. For X-ray diffraction studies, crystals were kept wet with supernatant solution. Crystals collected in the laboratory atmosphere, washed with ethanol (2 × 1 cm³), and dried by vacuum desiccation became opaque. Microanalyses were consistent with loss of solvent relative to the stoichiometry implied by the structure determination and the incorporation of water, presumably from the laboratory atmosphere (yield, 40–50%). [Tm(LH₂)A]·H₂O (Found: C, 57.6; H, 6.00; N, 5.40. Calc. for C₆₂H₈₀N₅O₁₄Tm: C, 57.8; H, 6.25; N, 5.45%).

L·2HA·EtOH. The calixarene L (0.025 mmol) was dissolved in dichloromethane (3 cm³). This solution was shaken with an excess of picric acid in water. The deep red organic layer was separated and dried (MgSO₄), and ethanol (2 cm³) was added. Upon slow evaporation of the dichloromethane, deep red crystals, appropriate for X-ray crystallographic studies, formed on the side of the flask, along with a fine white powder which hampered efforts to isolate the pure adduct (yield, 40–50%). L·2HA·EtOH (Found: C, 60.3; H, 6.6; N, 8.8. Calc. for C₇₀H₉₀N₈O₂₁: C, 60.95; H, 6.55; N, 8.1%).

Structure Determinations.—Crystals were prepared as described above and loaded in thin-walled capillaries. They decomposed rapidly in the absence of solvent and so the appropriate solvent was also included within the capillaries. Crystal data are given in Table 1, together with refinement details. Data for all four crystals [Tm(LH₂)A]·2.5CH₂Cl₂

1, [Ce(LH₂)(MeOH)₂A]·HA·H₂O 2, [PrLA₃]·2CH₂Cl₂·1.5H₂O 3 and L·2HA·EtOH 4 were collected with Mo-K α radiation using the MAR research image plate system. The crystals were positioned at 75 mm from the image plate and 95 frames were measured at 2° intervals with a counting time of 2 mins. Data analysis was carried out with the XDS program.¹⁷ The positions of the heavy atoms in structures 1, 2 and 3 were obtained from Patterson syntheses and remaining atoms were located from Fourier methods. The structure of compound 4 was determined by direct methods using SHELXS 86.¹⁸ All structures exhibited features of disorder, particularly in the *tert*-butyl groups at the top of the calix[4]arene cavity and in the nitro groups in the picrate anions. In addition the structures contained solvent molecules, some of which exhibited reduced occupancy.

All ordered non-hydrogen atoms in the complexes were refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon atoms were included in geometric positions with thermal parameters equivalent to 1.2 times the atom to which they were bonded. Methyl hydrogen atoms were refined as rigid groups. The majority of hydrogen atoms bonded to oxygen atoms could not be located in Fourier-difference maps and were not included. In complex 1 two of the *tert*-butyl groups were disordered and for each group, two sets of carbon atoms were refined with occupancies that added up to 1.0. One nitro group on the picrate anion had high thermal motion but a suitable disordered model could not be found. Three solvent dichloromethane molecules were located of which one was given an occupancy of 0.5. In complex 2 one solvent water molecule was located with full occupancy. Here one nitro group in the chelating picrate group, and all three in the free picric acid had high thermal motion but no satisfactory disordered model could be found. In complex 3 two solvent dichloromethane molecules were found. One was disordered in that two possible locations were found for each chlorine atom and these were refined with 50% occupancy. Three water molecules were located and given 50% occupancy. One of the nitro groups in a picrate anion was given a disordered model in which two

Table 2 Bond lengths in the metal co-ordination spheres of complexes 1, 2 and 3

		1	2	3
In the calixarene				
phenolic	M–O(250)	2.046(7)	2.473(7)	2.614(14)
phenolic	M–O(450)	2.116(6)	2.466(8)	—
ethereal	M–O(150)	2.406(6)	2.879(7)	—
ethereal	M–O(350)	2.440(5)	2.733(7)	—
carbonyl	M–O(153)	2.319(6)	2.503(8)	2.40(2)
carbonyl	M–O(353)	2.301(5)	2.479(8)	2.39(2)
In the picrates				
phenolic	M–O(50)	2.425(7)	2.495(8)	2.51(2)
nitro group	M–O(521)	2.631(7)	2.636(8)	2.52(2)
phenolic	M–O(60)	—	—	2.28(2)
nitro group	M–O(621)	—	—	2.74(2)
phenolic	M–O(70)	—	—	2.34(2)
nitro group	M–O(721)	—	—	2.78(2)
In the solvent				
methanol	M–O(70)	—	2.537(9)	—
	M–O(80)	—	2.598(9)	—

Table 3 Bond angles (°) in the co-ordination sphere of complex 1

O(250)–Tm–O(450)	98.3(3)
O(250)–Tm–O(353)	136.5(2)
O(450)–Tm–O(353)	91.8(2)
O(250)–Tm–O(153)	139.7(2)
O(450)–Tm–O(153)	90.9(2)
O(353)–Tm–O(153)	81.8(2)
O(250)–Tm–O(150)	79.1(2)
O(450)–Tm–O(150)	78.3(2)
O(353)–Tm–O(150)	144.4(2)
O(153)–Tm–O(150)	64.4(2)
O(250)–Tm–O(50)	85.6(3)
O(450)–Tm–O(50)	154.1(3)
O(353)–Tm–O(50)	102.9(2)
O(153)–Tm–O(50)	70.7(2)
O(150)–Tm–O(50)	77.4(2)
O(250)–Tm–O(350)	76.3(2)
O(450)–Tm–O(350)	78.7(2)
O(353)–Tm–O(350)	64.4(2)
O(153)–Tm–O(350)	144.0(2)
O(150)–Tm–O(350)	143.2(2)
O(50)–Tm–O(350)	126.8(2)
O(250)–Tm–O(521)	80.6(3)
O(450)–Tm–O(521)	143.2(2)
O(353)–Tm–O(521)	66.9(2)
O(153)–Tm–O(521)	113.8(2)
O(150)–Tm–O(521)	136.1(2)
O(50)–Tm–O(521)	62.6(2)
O(350)–Tm–O(521)	65.2(2)

positions for each oxygen atom were provided, each with 50% occupancy. In compound 4 one solvent ethanol molecule was located. One nitro group was disordered and two positions each with 50% occupancy were refined for each oxygen atom.

All structures were refined using SHELXL 93¹⁹ on an R4000 Workstation at the University of Reading. Dimensions in the metal co-ordination spheres are given in Tables 2 (bond lengths) and 3–5 (angles) and the final coordinates for 1–4 are given in Tables 6–9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

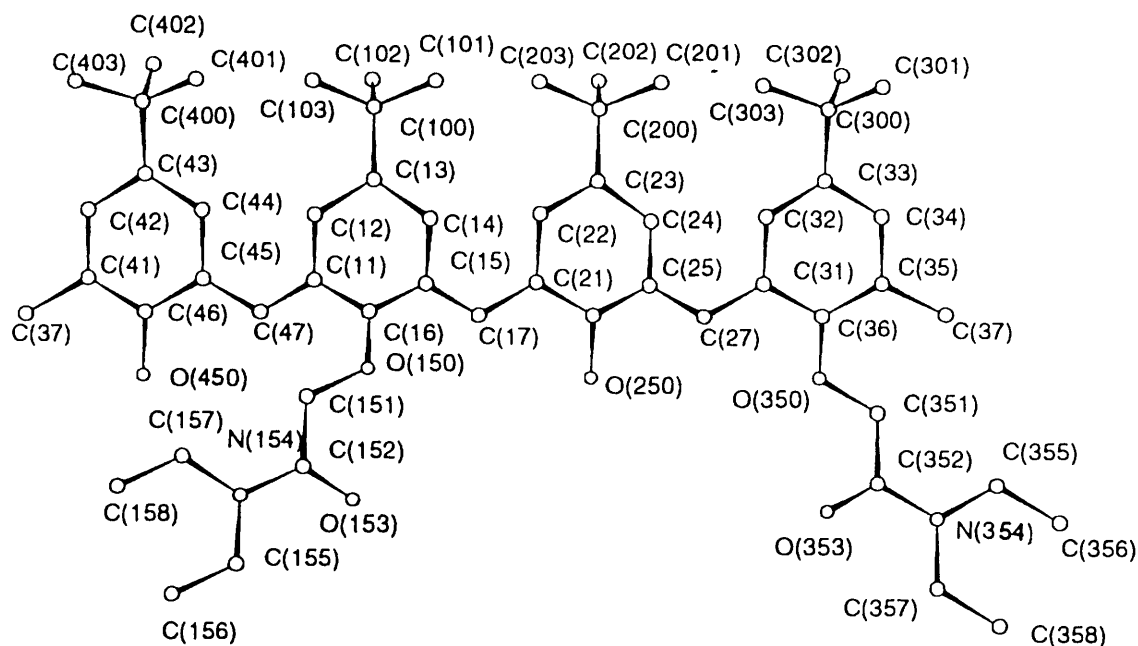
Results and Discussion

Lanthanide complexes of the calix[4]arene diamide (L), have been synthesised by combining L with the appropriate

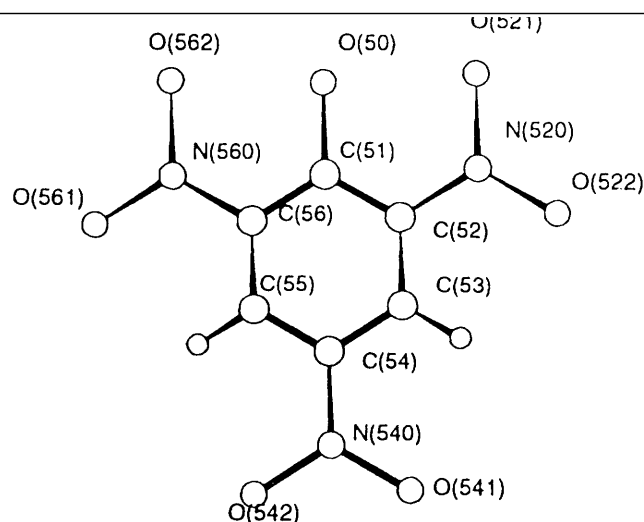
Table 4 Bond angles (°) in the co-ordination sphere of complex 2

O(450)–Ce–O(250)	65.5(2)
O(450)–Ce–O(353)	123.4(2)
O(250)–Ce–O(353)	107.8(2)
O(450)–Ce–O(50)	75.7(3)
O(250)–Ce–O(50)	132.1(3)
O(353)–Ce–O(50)	71.2(3)
O(450)–Ce–O(153)	116.6(2)
O(250)–Ce–O(153)	97.9(3)
O(353)–Ce–O(153)	119.9(2)
O(50)–Ce–O(153)	124.9(3)
O(450)–Ce–O(70)	139.1(3)
O(250)–Ce–O(70)	73.7(3)
O(353)–Ce–O(70)	66.2(3)
O(50)–Ce–O(70)	135.8(3)
O(153)–Ce–O(70)	70.9(3)
O(450)–Ce–O(80)	139.1(3)
O(250)–Ce–O(80)	154.4(3)
O(353)–Ce–O(80)	67.3(3)
O(50)–Ce–O(80)	71.6(3)
O(153)–Ce–O(80)	66.7(3)
O(70)–Ce–O(80)	81.7(3)
O(450)–Ce–O(521)	73.0(3)
O(250)–Ce–O(521)	125.3(2)
O(353)–Ce–O(521)	124.7(3)
O(50)–Ce–O(521)	62.7(3)
O(153)–Ce–O(521)	70.3(3)
O(70)–Ce–O(521)	138.7(3)
O(80)–Ce–O(521)	70.4(3)
O(450)–Ce–O(350)	69.1(2)
O(250)–Ce–O(350)	69.3(2)
O(353)–Ce–O(350)	57.5(2)
O(50)–Ce–O(350)	71.4(3)
O(153)–Ce–O(350)	163.1(3)
O(70)–Ce–O(350)	94.4(3)
O(80)–Ce–O(350)	120.5(3)
O(521)–Ce–O(350)	125.9(3)
O(450)–Ce–O(150)	62.5(2)
O(250)–Ce–O(150)	64.3(2)
O(353)–Ce–O(150)	168.3(3)
O(50)–Ce–O(150)	120.5(3)
O(153)–Ce–O(150)	55.8(2)
O(70)–Ce–O(150)	102.6(3)
O(80)–Ce–O(150)	115.8(3)
O(521)–Ce–O(150)	65.7(2)
O(350)–Ce–O(150)	122.9(2)

lanthanide picrate (2,4,6-trinitrophenolate) hydrates. Combining the calixarene and metal salt in a dichloromethane–ethanol solvent mixture results in isolation of orange crystalline complexes which give microanalytical results consistent with the formulation $[\text{LnLA}_3]$ (Ln = La, Ce, Pr or Eu). The UV/VIS spectra of these complexes in dichloromethane solution show two peaks consistent with the presence of co-ordinated picrate²⁰ [e.g. for the Pr complex: 410 ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$ cm^{-1} , 12 000) and 340 nm (28 000)]. The behaviour of the compounds upon recrystallisation from dichloromethane–methanol varies. The praseodymium and europium complexes are recovered apparently unchanged as orange crystals, while the lanthanum and cerium complexes give rise to dark brown solutions which deposit large dark brown crystals. Microanalytical results (and the ¹H NMR spectrum of the La complex) are consistent with the loss of one picrate relative to the starting material, to give the formulation $[\text{LnLA}_2]\cdot\text{MeOH}$. Consistent with the observed change in colour, the UV/VIS spectra show, in addition to the expected picrate absorbances at 410 and 340 nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$ cm^{-1} , 18 000 and 35 500), an absorbance at 315 nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$ cm^{-1} , 25 000). The presence of a base in the reaction mixture changes the nature of the product formed. Thus, if the lanthanide picrate and calixarene are combined in the presence of triethylamine, a dark brown solution is formed immediately and dark brown crystals are slowly deposited. The

**Table 5** Bond angles (°) in the co-ordination sphere of complex 3

O(60)–Pr–O(70)	132.4(7)
O(60)–Pr–O(353)	77.0(7)
O(70)–Pr–O(353)	92.3(6)
O(60)–Pr–O(153)	141.8(6)
O(70)–Pr–O(153)	74.0(6)
O(353)–Pr–O(153)	74.7(7)
O(60)–Pr–O(50)	88.4(7)
O(70)–Pr–O(50)	75.3(7)
O(353)–Pr–O(50)	146.3(6)
O(153)–Pr–O(50)	128.7(7)
O(60)–Pr–O(522)	127.9(6)
O(70)–Pr–O(522)	85.7(6)
O(353)–Pr–O(522)	145.7(7)
O(153)–Pr–O(522)	71.9(6)
O(50)–Pr–O(522)	65.8(6)
O(60)–Pr–O(250)	86.4(6)
O(70)–Pr–O(250)	138.7(6)
O(353)–Pr–O(250)	82.5(5)
O(153)–Pr–O(250)	65.1(5)
O(50)–Pr–O(250)	127.3(5)
O(522)–Pr–O(250)	76.8(5)
O(60)–Pr–O(621)	61.1(5)
O(70)–Pr–O(621)	135.3(6)
O(353)–Pr–O(621)	130.3(5)
O(153)–Pr–O(621)	124.1(5)
O(50)–Pr–O(621)	61.7(5)
O(522)–Pr–O(621)	66.8(5)
O(250)–Pr–O(621)	70.1(5)
O(60)–Pr–O(721)	71.2(7)
O(70)–Pr–O(721)	61.2(7)
O(353)–Pr–O(721)	76.4(6)
O(153)–Pr–O(721)	124.7(6)
O(50)–Pr–O(721)	70.1(6)
O(522)–Pr–O(721)	130.2(6)
O(250)–Pr–O(721)	152.0(6)
O(621)–Pr–O(721)	110.7(6)



that the addition of picric acid to a dichloromethane solution of **L** gave rise to a deep red solution [the UV/VIS spectrum showing an absorbance in the visible region at 335 nm (broad peak), with a weak shoulder at 405 nm], from which dark red crystals deposited after addition of ethanol. In order to elucidate the nature of this compound and the various lanthanide complexes in more detail, X-ray crystallographic studies were undertaken, the results of which are discussed below.

The structures of the four compounds have a common numbering scheme and are illustrated in Figs. 1–8 respectively; $[M(LH_2)A]$ ($M = Tm$ **1**) is illustrated in Fig. 1. It forms part of a series ($M = Lu, Yb$ or Er) whose structures are isomorphous to **1** (for $M = Sm$ or Pr the structures are equivalent, isomorphous to each other but not to **1**).²¹ In all these structures ($M = Lu, Yb, Er, Sm, Pr$ or Tm) the calix[4]arene diamide takes up the cone conformation so that the six oxygen atoms in the lower rim, two from the deprotonated phenolic oxygen atoms O(250), O(450), two from the ethereal oxygen atoms O(150), O(350) and two from the amide oxygen atoms O(153), O(353) are all available for bond formation. This contrasts with the crystal structure of the potassium complex of **L**, where the calixarene is found in the

analysis of these complexes is consistent with the formulation $[Ln(LH_2)A]$. The thulium complex is taken as an example here, and the full series will be described in detail elsewhere.²¹ Once again, the UV/VIS spectrum shows three peaks in the visible region, at 405 ($\epsilon/dm^3 mol^{-1} cm^{-1}$, 8500), 335 (16 500) and 315 nm (19 000). In the course of these studies, it was noted

Table 6 Atomic coordinates ($\times 10^4$) for complex 1

Atom	x	y	z	Atom	x	y	z
Tm	1353.7(1)	1925.0(2)	2640.8(2)	C(404)*	250(21)	3103(20)	-1758(16)
C(11)	-233(6)	4355(6)	1657(5)	C(405)*	-731(17)	2008(16)	-1472(13)
C(12)	-1159(8)	4915(6)	1506(7)	C(406)*	-1480(23)	3653(22)	-1058(18)
C(13)	-1966(8)	5273(7)	2060(7)	O(350)	887(4)	540(4)	2431(3)
C(14)	-1834(7)	4964(7)	2782(7)	O(450)	1044(5)	2124(4)	1536(4)
C(15)	-956(6)	4396(5)	2962(6)	C(351)	1613(6)	-338(5)	2362(6)
C(16)	-146(7)	4125(5)	2395(6)	C(352)	2638(6)	-187(5)	2269(5)
C(17)	-888(7)	4044(7)	3752(6)	O(353)	2677(4)	603(4)	2304(4)
C(21)	-1389(7)	3308(7)	3954(6)	N(354)	3446(6)	-894(5)	2179(5)
C(22)	-2252(8)	3476(7)	4466(6)	C(355)	3457(8)	-1857(7)	2097(9)
C(23)	-2705(8)	2797(8)	4685(6)	C(356)	3723(14)	-2172(13)	1316(12)
C(24)	-2251(7)	1922(8)	4376(6)	C(357)	4442(7)	-741(8)	2143(9)
C(25)	-1370(7)	1709(7)	3862(5)	C(358)	4682(13)	-665(15)	2876(12)
C(26)	-944(6)	2412(6)	3656(5)	O(150)	803(4)	3592(4)	2568(4)
C(27)	-858(7)	732(6)	3574(5)	C(151)	1469(7)	4101(5)	2626(6)
C(31)	-858(6)	623(6)	2755(5)	C(152)	2516(6)	3421(5)	2574(6)
C(32)	-1743(7)	600(6)	2501(6)	O(153)	2627(4)	2611(4)	2376(4)
C(33)	-1822(7)	538(6)	1769(6)	N(154)	3263(6)	3667(6)	2701(6)
C(34)	-981(7)	533(6)	1255(6)	C(155)	4256(8)	2973(9)	2699(9)
C(35)	-81(6)	558(5)	1451(5)	C(156)	4309(12)	2445(15)	3395(11)
C(36)	-27(6)	565(5)	2218(5)	C(157)	3184(10)	4632(9)	2923(10)
C(37)	752(7)	608(6)	852(5)	C(158)	3656(16)	5110(12)	2336(14)
C(41)	524(6)	1570(6)	528(5)	O(250)	-99(5)	2230(4)	3176(4)
C(42)	147(7)	1750(6)	-125(5)	O(50)	1730(6)	2400(5)	3794(4)
C(43)	-99(7)	2629(7)	-437(6)	C(51)	1215(8)	2398(7)	4415(5)
C(44)	62(7)	3323(6)	-54(5)	C(52)	835(8)	1676(7)	4726(6)
C(45)	447(6)	3179(6)	621(5)	C(53)	164(8)	1775(8)	5366(5)
C(46)	684(6)	2282(6)	920(5)	C(54)	-142(8)	2573(8)	5759(6)
C(47)	603(7)	3954(6)	1026(5)	C(55)	287(11)	3274(8)	5560(6)
C(100)*	-2934(10)	5987(9)	1898(9)	C(56)	978(9)	3137(7)	4911(6)
C(101)*	-2764(24)	6843(22)	1618(19)	N(521)	1191(7)	773(6)	4344(5)
C(102)*	-3821(25)	6182(24)	2552(19)	O(521)	1628(6)	699(5)	3709(4)
C(103)*	-3364(25)	5569(23)	1313(19)	O(522)	1058(8)	112(6)	4705(5)
C(104)*	-3042(36)	6875(32)	2310(28)	N(541)	-918(9)	2725(9)	6389(6)
C(105)*	-3787(26)	5638(26)	2134(21)	O(541)	-1253(9)	2095(9)	6580(6)
C(106)*	-2945(40)	6152(38)	1097(29)	O(542)	-1196(9)	3478(8)	6709(5)
C(200)	-3703(11)	3038(11)	5230(8)	N(561)	1484(11)	3862(8)	4730(7)
C(201)	-3931(25)	2221(18)	5527(22)	O(561)	2305(14)	3704(13)	4761(19)
C(202)	-4529(15)	3590(28)	4824(17)	O(562)	1065(16)	4557(12)	4491(11)
C(203)	-3679(20)	3639(24)	5851(14)	C(61)	-2091(10)	2939(8)	1970(10)
C(300)	-2771(7)	429(8)	1525(7)	Cl(62)	-3122(3)	3188(4)	2627(3)
C(301)	-3697(8)	969(12)	2016(10)	Cl(63)	-2308(5)	3077(4)	1082(4)
C(302)	-2717(11)	-597(10)	1556(11)	C(71)	3277(17)	1969(23)	592(16)
C(303)	-2866(11)	720(16)	719(9)	Cl(72)	3815(12)	2843(11)	576(6)
C(400)	-516(9)	2807(7)	-1163(6)	Cl(73)	4073(10)	974(10)	246(7)
C(401)*	-750(28)	3717(24)	-1427(20)	C(81)*	3431(40)	1486(37)	5539(31)
C(402)*	-1398(24)	2349(23)	-1151(19)	Cl(82)*	2611(16)	1452(15)	6222(12)
C(403)*	204(25)	2169(23)	-1789(19)	Cl(83)*	3482(18)	457(17)	5053(14)

* 50% Occupancy.

1,3-alternate conformation, with the metal atom environment consisting of the two ethereal O atoms, the two amide O atoms, and two of the calixarene phenyl rings.²² This donor set of six can be expanded by further co-ordination. In [Tm(LH₂)A], the metal atom is eight-co-ordinate being bonded to these six oxygen atoms of the calix[4]arene diamide together with two oxygen atoms from a picrate anion. The shortest bonds, Tm–O(250) [2.046(7) Å] and Tm–O(450) [2.116(6) Å], are to the oxygen atoms at the bottom of the calix[4]arene rim, with associated C(n6)–O(n50)–Tm angles close to 180°. A search of the Cambridge Crystallographic Database shows that these Tm–O distances are among the shortest thulium-to-oxygen bond lengths known. The next shortest bonds are to the two amide oxygen atoms Tm–O(153) 2.319(6) and Tm–O(353) 2.301(5) Å. Here the C(n52)–O(n53)–La angles are *ca.* 120°. Next in length come the bonds to the ethereal O atoms at the bottom of the calix[4]arene rim [Tm–O(150) 2.406(6), Tm–O(350) 2.440(5) Å] and to the picrate anion. The picrate is bonded to the metal in a bidentate fashion *via* the phenolic O atom [Tm–O(50) 2.425(7) Å] and a nitro oxygen [Tm–O(521) 2.631(7)

Å]. As might be expected the bond to the O[–] ion is significantly shorter than to the nitro oxygen atom. The six-membered chelate ring subtended by the picrate anion is not planar; the angle of intersection between the Tm, O(50), O(521) plane and the O(50), O(521), C(51), C(52), N(52) plane is 45.4°. This tilt in the picrate with respect to the donor atoms gives rise to the phenyl ring being approximately parallel to phenyl ring 2 on the calix[4]arene. The angle of intersection is 18.4° and the closest approach [between C(51) and C(26)] is 3.41 Å. The three nitro groups are not coplanar with the picrate, with angles of intersection of 19.4, 7.2 and 70.9° for the nitro groups on C(52), C(54) and C(56) respectively. The position of the picrate anion suggests that the intense colour of the complex may be due to a charge-transfer absorbance between the calixarene and picrate moieties. This feature of the structure is emphasised in Fig. 2, which shows a space-filling close-up of the interaction.

The co-ordination sphere of the thulium atom is best described as a distorted square antiprism. The four oxygen atoms [O(n50), *n* = 1–4] at the bottom rim of the calix[4]arene form one plane (root mean square deviation 0.30 Å), while the

Table 7 Atomic coordinates ($\times 10^4$) for complex **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ce	1839.5(5)	3471.4(5)	1965.7(2)	C(156)	7791(20)	759(18)	1639(8)
C(11)	3605(11)	2607(9)	3354(4)	C(157)	5565(16)	989(14)	980(5)
C(12)	3347(13)	2429(10)	3836(4)	C(158)	5045(29)	123(23)	813(9)
C(13)	2763(14)	1629(11)	4021(4)	O(350)	−550(7)	4588(6)	2334(2)
C(14)	2380(12)	1069(10)	3696(4)	C(351)	−1359(11)	5190(10)	2048(4)
C(15)	2560(10)	1206(8)	3207(4)	C(352)	−721(11)	4973(9)	1533(4)
C(16)	3203(9)	1962(8)	3035(4)	O(353)	254(7)	4313(6)	1446(2)
C(17)	2028(10)	585(8)	2855(4)	N(354)	−1271(11)	5502(8)	1182(3)
C(21)	607(11)	844(8)	2908(4)	C(355)	−615(17)	5293(13)	677(4)
C(22)	−142(12)	171(10)	3098(4)	C(356)	435(23)	5813(17)	567(6)
C(23)	−1462(13)	402(10)	3147(4)	C(357)	−2434(22)	6256(16)	1248(6)
C(24)	−2041(12)	1339(9)	2991(4)	C(358)	−2547(36)	7184(28)	1194(13)
C(25)	−1336(11)	2035(9)	2788(4)	O(250)	698(7)	2487(5)	2576(3)
C(26)	−13(10)	1785(8)	2751(4)	O(450)	1795(7)	4008(6)	2808(3)
C(27)	−1991(10)	3058(9)	2637(4)	C(51)	2610(13)	5955(9)	1977(4)
C(31)	−1800(10)	3868(9)	2962(4)	C(52)	3893(11)	5725(9)	2076(4)
C(32)	−2233(11)	3831(10)	3451(4)	C(53)	4569(14)	6456(12)	2163(4)
C(33)	−1973(13)	4491(12)	3786(4)	C(54)	4050(15)	7447(12)	2128(5)
C(34)	−1232(13)	5181(11)	3618(5)	C(55)	2829(18)	7770(12)	2011(6)
C(35)	−785(11)	5239(9)	3139(4)	C(56)	2102(15)	7045(11)	1946(5)
C(36)	−1091(10)	4602(9)	2816(3)	O(50)	1916(8)	5324(6)	1915(3)
C(37)	112(13)	5975(10)	2961(5)	N(540)	4758(18)	8217(14)	2191(5)
C(41)	1410(13)	5713(10)	3133(4)	O(541)	4244(15)	9113(13)	2135(6)
C(42)	1900(14)	6450(9)	3336(4)	O(542)	5849(19)	7955(14)	2292(6)
C(43)	3055(16)	6273(10)	3491(4)	N(520)	4590(10)	4666(8)	2105(4)
C(44)	3781(14)	5276(10)	3439(5)	O(521)	4086(8)	3977(7)	2016(3)
C(45)	3387(12)	4493(8)	3224(4)	O(522)	5683(9)	4541(8)	2200(4)
C(46)	2192(11)	4732(8)	3063(4)	N(560)	859(15)	7417(11)	1829(6)
C(47)	4242(12)	3472(9)	3160(5)	O(561)	351(23)	6963(14)	1639(12)
C(100)	2606(21)	1426(14)	4548(6)	O(562)	223(22)	8106(22)	2053(13)
C(101)	3341(43)	538(31)	4667(14)	C(61)	−508(21)	2164(13)	362(6)
C(102)	1080(42)	1138(34)	4681(14)	C(62)	−1885(19)	2611(16)	412(7)
C(103)	2363(50)	2197(38)	4811(16)	C(63)	−2721(28)	2595(20)	78(10)
C(200)	−2292(14)	−372(12)	3373(6)	C(64)	−2224(34)	2004(26)	−331(10)
C(202)	−3626(38)	−50(31)	3399(13)	C(65)	−1106(41)	1491(21)	−380(9)
C(203)	−1665(44)	−1033(33)	3713(14)	C(66)	−228(27)	1530(15)	−82(6)
C(201)	−2107(47)	−1226(34)	2970(15)	O(60)	212(13)	2306(10)	619(4)
C(300)	−2375(17)	4345(17)	4325(5)	N(620)	−2365(20)	3283(19)	857(11)
C(301)	−3641(24)	4056(20)	4438(8)	O(621)	−1896(23)	3157(16)	1211(7)
C(302)	−2402(38)	5248(28)	4611(12)	O(622)	−3203(31)	3951(29)	810(13)
C(303)	−1433(38)	3490(28)	4501(12)	N(640)	−3195(33)	1916(25)	−633(12)
C(400)	3552(20)	7122(13)	3742(6)	O(641)	−4190(36)	2529(33)	−628(16)
C(401)	5162(31)	6960(25)	3571(11)	O(642)	−2749(32)	1419(23)	−994(9)
C(402)	3349(30)	7055(23)	4250(9)	N(660)	1064(25)	906(17)	−199(10)
C(403)	3179(21)	8088(16)	3510(7)	O(661)	1754(33)	675(25)	129(15)
O(150)	3462(7)	2133(6)	2543(2)	O(662)	1288(35)	460(30)	−532(10)
C(151)	4630(10)	1507(9)	2317(4)	O(70)	941(9)	2230(7)	1500(3)
C(152)	4609(9)	1527(8)	1791(4)	C(71)	1183(16)	1160(13)	1506(6)
O(153)	3655(8)	2042(6)	1630(3)	O(80)	2934(9)	3814(8)	1105(3)
N(154)	5583(10)	978(8)	1496(3)	C(81)	3700(37)	4484(32)	915(10)
C(155)	6661(13)	301(13)	1658(5)	Ow(1)	2284(22)	2982(17)	313(7)

other donor atoms O(153), O(353), O(50), O(521) form another (root mean square deviation 0.05 Å). These two planes are approximately parallel with an angle of intersection of 1.7°. A view of the co-ordination sphere looking down the cavity is shown in Fig. 3. These two planes of four oxygen atoms are also approximately parallel to the plane of the four methylene carbon atoms [C(*n*7), *n* = 1–4] (angles of intersection 4.4, 4.7°). The cone of the calix[4]arene is significantly distorted from *C*₄ symmetry in that the angles made by the phenyl rings with the plane of the four methylene atoms are 69.6, 33.0, 71.7 and 45.5°, the conformation thus having approximate *C*₂ symmetry. This is of course expected for a calix[4]arene substituted at the 1,3 positions at the bottom of the cone. Thus the 1 and 3 rings are more vertical with respect to the cone axis than the unsubstituted 2 and 4 rings.

The structure of the complex [Ce(LH_{−2})(MeOH)₂A] **2** is shown in Fig. 4. The structure of the lanthanum complex is isomorphous and the dimensions are very similar (all La–O bond lengths are within 0.05 Å of the Ce–O bond lengths in **2**) but

the crystal quality is poor and the structure is not reported here in detail.*

The cerium atom is ten-co-ordinate being bonded to the six oxygen atoms of the calix[4]arene diamide, to a bidentate picrate anion and to two methanol molecules. There is also a water molecule and a picrate moiety in the asymmetric unit which participate in intermolecular hydrogen bonding. The metal–oxygen bond lengths are less disparate than in the thulium complex. Thus the bonds to O(250) and O(450) [2.473(7) and 2.466(8) Å] are equivalent to those to the amide oxygen atoms O(353) and O(153) [2.479(8) and 2.503(8) Å]. The bond lengths to the bidentate picrate are O(50) 2.495(8), O(521) 2.636(8) Å and to the methanol molecules are O(70) 2.537(9), O(80) 2.598(9) Å. The longest bonds are to the two ethereal

* [La(LH_{−2})(MeOH)₂A]·HA·H₂O, triclinic, space group *P* $\bar{1}$, *a* = 10.701(8), *b* = 13.373(8), *c* = 27.964(9), α = 89.47(1), β = 81.67(1), γ = 78.17(1), *U* = 3874.6 Å³.

Table 8 Atomic coordinates ($\times 10^4$) for complex **3**

Atom	x	y	z	Atom	x	y	z
Pr	2 220.7(6)	10 124.8(7)	1 780.3(4)	C(157)	-1 511(28)	8 410(19)	1 087(11)
C(11)	-1 369(24)	7 363(26)	2 953(9)	C(158)	-2 223(30)	9 283(41)	786(19)
C(12)	-1 929(19)	7 094(21)	3 380(9)	C(51)	1 168(23)	12 674(20)	1 681(9)
C(13)	-1 789(23)	7 676(23)	3 788(10)	C(52)	142(19)	12 583(18)	1 852(8)
C(14)	-1 140(22)	8 466(22)	3 708(10)	C(53)	-635(21)	13 394(19)	1 846(9)
C(15)	-620(21)	8 708(17)	3 267(9)	C(54)	-367(27)	14 320(24)	1 667(12)
C(16)	-778(21)	8 188(20)	2 893(9)	C(55)	609(27)	14 516(21)	1 474(9)
C(17)	96(18)	9 583(20)	3 207(9)	C(56)	1 329(25)	13 791(23)	1 498(8)
C(21)	1 271(17)	9 250(17)	3 381(7)	O(50)	1 994(18)	12 038(14)	1 666(6)
C(22)	1 507(18)	9 234(20)	3 867(8)	N(520)	-181(20)	11 616(17)	2 062(7)
C(23)	2 619(19)	8 932(21)	4 045(9)	O(522)	428(14)	10 854(14)	2 063(6)
C(24)	3 332(27)	8 513(25)	3 727(8)	O(521)	-1 051(18)	11 533(17)	2 237(10)
C(25)	3 076(16)	8 458(16)	3 258(8)	N(540)	-1 283(32)	15 171(17)	1 645(9)
C(26)	2 023(19)	8 893(19)	3 092(8)	O(541)	-2 160(18)	15 051(16)	1 798(10)
C(27)	3 844(27)	7 949(21)	2 992(11)	O(542)	-1 025(17)	16 046(17)	1 433(8)
C(31)	3 738(18)	6 781(15)	3 028(8)	N(560)	2 476(23)	14 029(25)	1 294(9)
C(32)	4 178(23)	6 186(27)	3 448(9)	O(561)	3 169(24)	13 418(33)	1 357(27)
C(33)	3 999(17)	5 064(18)	3 554(9)	O(562)	2 576(30)	14 859(37)	1 135(16)
C(34)	3 393(20)	4 771(21)	3 179(9)	C(61)	4 520(21)	10 278(18)	2 467(10)
C(35)	3 137(21)	5 310(15)	2 770(8)	C(62)	4 109(26)	10 815(20)	2 867(8)
C(36)	3 233(18)	6 341(21)	2 676(7)	C(63)	4 882(27)	10 985(23)	3 205(13)
C(37)	2 286(15)	4 917(18)	2 440(8)	C(64)	5 904(22)	10 526(26)	3 245(12)
C(41)	1 163(21)	4 911(21)	2 635(8)	C(65)	6 280(24)	10 056(23)	2 880(11)
C(42)	994(20)	4 047(26)	2 964(9)	C(66)	5 576(22)	9 818(27)	2 535(11)
C(43)	-164(19)	4 015(23)	3 181(10)	O(60)	3 886(14)	10 128(15)	2 122(6)
C(44)	-798(22)	4 805(25)	3 021(11)	N(620)	3 013(16)	11 196(23)	2 890(8)
C(45)	-601(20)	5 739(18)	2 717(10)	O(621)	2 380(12)	10 982(12)	2 608(6)
C(46)	460(19)	5 705(19)	2 509(9)	O(622)	2 813(19)	11 853(23)	3 122(12)
C(47)	-1 436(20)	6 638(22)	2 582(10)	N(640)	6 629(27)	10 735(26)	3 613(11)
C(100)	-2 402(26)	7 319(26)	4 248(12)	O(641)	7 563(25)	10 521(23)	3 566(10)
C(101)	-3 761(37)	7 400(50)	4 160(23)	O(642)	6 207(26)	11 167(27)	3 928(12)
C(102)	-2 037(42)	6 189(36)	4 441(19)	N(660)	6 012(23)	9 238(22)	2 162(10)
C(103)	-2 072(41)	7 907(33)	4 663(15)	O(661)*	6 670(48)	9 501(50)	1 876(23)
C(200)	2 868(14)	9 241(27)	4 584(10)	O(662)*	5 755(73)	8 413(39)	2 242(32)
C(201)	3 735(33)	9 940(37)	4 532(19)	O(663)*	5 728(46)	9 499(40)	1 750(14)
C(202)	1 945(34)	9 437(35)	4 863(13)	O(664)*	6 360(63)	8 396(33)	2 333(20)
C(203)	3 370(42)	8 004(30)	4 858(10)	C(71)	1 486(36)	11 494(25)	699(8)
C(300)	4 445(38)	4 350(39)	4 004(11)	C(72)	2 332(32)	12 017(25)	492(10)
C(301)	3 992(33)	3 322(27)	4 122(13)	C(73)	2 366(36)	12 929(26)	178(11)
C(302)	5 635(29)	4 180(51)	4 000(18)	C(74)	1 292(52)	13 438(21)	12(11)
C(303)	4 234(48)	4 850(35)	4 455(14)	C(75)	363(32)	13 041(20)	165(10)
C(400)	-405(27)	3 176(24)	3 545(14)	C(76)	464(29)	12 115(29)	489(11)
C(401)	375(70)	3 082(71)	3 992(20)	O(70)	1 521(18)	10 694(15)	965(6)
C(402)	-1 349(70)	3 343(41)	3 848(31)	N(720)	3 477(31)	11 561(21)	664(8)
C(403)	-518(101)	2 334(59)	3 348(26)	O(722)	4 124(39)	11 714(26)	393(11)
O(250)	1 842(13)	8 804(12)	2 588(5)	O(721)	3 580(19)	10 959(18)	1 030(9)
O(450)	696(12)	6 579(14)	2 174(6)	N(740)	1 165(32)	14 394(19)	-352(13)
O(350)	2 882(13)	6 977(13)	2 230(5)	O(741)	307(27)	14 749(23)	-487(10)
C(351)	3 556(11)	6 859(12)	1 812(5)	O(742)	1 934(29)	14 821(28)	-438(18)
C(352)	3 651(22)	7 907(23)	1 488(8)	N(760)	-499(31)	11 652(27)	675(10)
O(353)	3 222(16)	8 661(14)	1 558(6)	O(761)	-1 327(30)	11 756(38)	350(12)
N(354)	4 269(20)	7 795(19)	1 096(8)	O(762)	-609(24)	11 268(23)	1 085(8)
C(355)	4 841(31)	6 929(29)	952(11)	C(800)	1 390(31)	6 628(31)	4 090(13)
C(356)	6 030(36)	6 638(31)	1 167(15)	Cl(81)	1 012(18)	5 847(18)	3 788(8)
C(357)	4 434(31)	8 783(26)	734(10)	Cl(82)	1 158(19)	6 249(20)	4 696(8)
C(358)	3 645(27)	9 050(31)	365(12)	C(83)	5 309(101)	3 954(102)	2 587(46)
O(150)	-183(14)	8 444(14)	2 431(5)	Cl(85A)*	6 041(43)	5 238(44)	2 549(19)
C(151)	-777(24)	8 922(21)	2 035(8)	Cl(84A)*	6 664(56)	3 156(54)	2 667(24)
C(152)	-103(28)	8 834(21)	1 599(9)	Cl(85B)*	5 068(49)	4 146(52)	1 967(24)
O(153)	903(11)	8 999(13)	1 676(6)	Cl(84B)*	4 942(87)	2 880(94)	2 258(40)
N(154)	-373(16)	8 657(15)	1 170(6)	Ow(1)*	4 700(77)	5 809(74)	-464(32)
C(155)	374(24)	8 571(19)	790(10)	Ow(2)*	3 084(65)	6 709(66)	-959(29)
C(156)	1 111(25)	7 595(25)	855(13)	Ow(3)*	3 519(76)	7 931(77)	-1 465(35)

* 50% Occupancy.

oxygen atoms O(150) 2.879(7) and O(350) 2.733(7) Å. The conformation of the calixarene in this ten-co-ordinate complex is similar to that observed in the eight-co-ordinate complex **1**. In the calix[4]arene the phenyl rings intersect the plane of the methylene C atoms [C(*n*7), *n* = 1–4] at angles of 78.6, 33.5, 89.7 and 15.3°. The distortion from *C*₄ symmetry is similar to

that observed in complex **1** but slightly greater. The two planes of donor atoms O(150), O(250), O(350), O(450) and O(153), O(353), O(50), O(521) are similarly parallel to the methylene plane (angles of intersection 3.5 and 14.7°). The arrangement of these eight oxygen atoms around the metal is similar to that observed in **1**, but in addition two solvent methanol molecules

Table 9 Atomic coordinates ($\times 10^4$) for complex **4**

Atom	x	y	z
C(11)	3 323(5)	1 324(7)	9 269(4)
C(12)	3 315(6)	2 116(7)	9 773(5)
C(13)	2 560(6)	2 502(7)	10 083(5)
C(14)	1 862(6)	2 010(7)	9 857(5)
C(15)	1 854(5)	1 204(6)	9 334(5)
C(16)	2 596(5)	835(6)	9 083(4)
C(17)	1 015(5)	821(7)	9 051(5)
C(21)	744(5)	1 345(6)	8 284(5)
C(22)	403(6)	2 305(8)	8 312(7)
C(23)	184(6)	2 849(8)	7 642(7)
C(24)	335(5)	2 375(7)	6 924(6)
C(25)	687(5)	1 407(7)	6 859(5)
C(26)	853(5)	892(7)	7 555(5)
C(27)	863(5)	953(7)	6 059(5)
C(100)	2 551(7)	3 389(9)	10 669(6)
C(101)	3 321(14)	3 952(23)	10 713(20)
C(102)	1 961(19)	4 187(17)	10 348(15)
C(103)	2 228(22)	3 068(14)	11 418(9)
C(200)	−199(9)	3 889(10)	7 699(8)
C(201)	−119(13)	4 363(12)	8 515(12)
C(202)	−1 095(9)	3 803(12)	7 413(11)
C(203)	267(13)	4 594(11)	7 123(14)
O(150)	2 637(4)	−8(4)	8 585(3)
C(151)	2 410(6)	−964(7)	8 919(6)
C(152)	3 092(7)	−1 728(9)	8 860(6)
O(153)	3 779(5)	−1 463(6)	8 619(6)
N(154)	2 948(6)	−2 681(7)	9 083(6)
C(155)	3 597(10)	−3 427(10)	9 034(10)
C(156)	4 148(11)	−3 438(13)	9 738(10)
C(157)	2 150(10)	−2 984(11)	9 330(11)
C(158)	1 660(13)	−3 549(14)	8 776(19)
O(250)	1 123(4)	−96(4)	7 562(4)
C(51)	717(7)	711(11)	2 949(8)
C(52)	566(7)	901(10)	2 178(8)
C(53)	791(7)	301(11)	1 574(8)
C(54)	1 231(6)	−553(11)	1 796(7)
C(55)	1 421(6)	−766(11)	2 535(7)
C(56)	1 192(7)	−137(13)	3 125(6)
O(50)	453(6)	1 226(10)	3 589(7)
N(520)	97(9)	1 778(12)	1 947(10)
O(521)	−65(9)	2 408(9)	2 459(9)
O(522)	−84(9)	1 922(12)	1 243(9)
N(540)	1 421(8)	−1 257(10)	1 136(8)
O(541)	1 150(7)	−1 106(10)	485(6)
O(542)	1 922(8)	−1 928(11)	1 287(7)
N(560)	1 468(9)	−387(12)	3 947(8)
O(561)*	2 098(9)	−14(11)	4 144(9)
O(562)*	1 134(23)	−922(36)	4 395(24)
O(563)*	1 383(16)	−1 378(16)	4 052(17)
O(564)*	950(16)	−124(21)	4 454(16)
C(600)	2 500	3 145(18)	7 500
C(601)	2 513(8)	3 772(11)	8 267(8)
O(602)	2 513(8)	3 772(11)	8 267(8)

* 50% Occupancy.

are co-ordinated; O(70) is inserted between the two planes so that the Ce–O(70) vector is approximately parallel to both of them. The second methanol group has a unique position so that O(80) is in a position capping the O(153), O(353), O(50), O(521) plane with the Ce–O(80) vector perpendicular to that plane. This additional co-ordination may be due to the larger size of the cerium and lanthanum atoms compared to the heavier lanthanide cations; as noted above, the analogous praseodymium complex does not form under similar reaction conditions, suggesting that slight changes in the cation size can strongly influence the nature of the complex formed.

Once again, the picrate phenyl ring is approximately parallel to a calixarene phenyl ring (ring 2), with an angle of intersection of 18.3° and a closest approach of 3.46 Å between C(51) and C(26). In this case, however, the chelate ring subtended by the picrate is approximately planar with the angle between Ce,

Table 10 Intermolecular hydrogen bonds (Å) in complexes **2** and **4**

2		4	
Ow(1) ... O(80)	2.74	O(153) ... O(521)	2.94
Ow(1) ... O(60)	2.61	O(50) ... O(521)	2.56
O(60) ... O(70)	2.70	O(153) ... O(250)	2.70
		O(250) ... O(150)	2.80

O(50) and O(521) and the plane of atoms O(50), O(521), N(520), C(51) and C(52) being 9.3°. The angle between the nitro groups and the phenyl ring in the metal-bound picrate are 3.3, 31.2 and 34.7° and in the free picrate are 24.9, 7.5 and 13.3° respectively.

The charge distribution in this system is not obvious. It appears that the cerium ion is tripositive (particularly as the La structure is isomorphous), contrasting with the cerium(III) complexes of unsubstituted *p*-tert-butylcalixarenes which readily oxidise to cerium(IV) in the normal laboratory atmosphere.^{13,23} There are a number of possibilities for the distribution of negative charge. It is likely that the bidentate picrate is anionic. The bond lengths to the two phenolic oxygen atoms at the bottom of the rim are similar to those to the two amide oxygen atoms. This is very different from the situation in the Tm complex where the M–O(*n*50) bonds are *ca.* 0.2 Å shorter than the M–O(*n*53) bonds. This could indicate that the O(*n*50) atoms in complex **2** are protonated rather than being anionic, and if that were the case, then the two OMe groups may be negatively charged. These M–O(methanol) distances are even longer, however, and on balance we think it more likely that the phenolic O(*n*50) atoms are ionic, and are lengthened by comparison with those in complex **1** because of effects of the increased co-ordination number and steric constraints. Additional evidence is provided by the structure of complex **3**, where the Pr–O distance to the presumably protonated oxygen atom at the bottom of the cone is 2.61(2) Å, significantly longer than to the two amide oxygen atoms [2.39(2) and 2.40(2) Å]. This discussion assumes that the second picric moiety in the unit cell of the cerium complex is the neutral species rather than the anion {both possibilities have been observed in [ScA(OH)₂]₄·A·HA, for example²⁴}. It is also possible that this moiety is anionic, with only one of the methanol or phenolic O atoms being deprotonated; examples of co-ordination of both RO[−] and ROH are well established.²⁵ The phenolic O atom, O(60), of the unattached picric moiety is within hydrogen-bonding distance of the water molecule (2.61 Å) (Table 10) and the methanol O(70) atom (2.70 Å). In addition there may be a hydrogen bond between the water molecule and the second methanol O(80) atom (2.74 Å). Details are shown in Fig. 5. It is also possible that the proton on O(60) forms an intramolecular hydrogen bond to one of the adjacent nitro groups.

The structure of [PrLA₃] is shown in Fig. 6. The metal atom is nine-co-ordinate, bonded to three picrate anions, all in a bidentate fashion. The additional three O atoms are provided by the calixarene; one (presumably protonated) phenolic O atom [Pr–O(250) 2.61(2) Å] at the bottom of the calix[4]arene rim and two amide oxygen atoms [Pr–O(153) 2.40(2), Pr–O(353) 2.39(2) Å]. It is interesting that while in two of the picrates, the bonds to the anionic oxygen atom [Pr–O(60) 2.28(2), Pr–O(70) 2.34(2) Å] are significantly shorter than the bonds to the nitro oxygen atom [Pr–O(621) 2.74(2), Pr–O(721) 2.78(2) Å] in the other, the bonds are equivalent within experimental error [Pr–O(50) 2.51(2), Pr–O(521) 2.52(2) Å]. This variation may be due to steric crowding about the metal centre, but it is also possible that the latter picrate is in fact protonated, in which case the phenolic O atom O(250) bonded to the metal would presumably be deprotonated.

Despite the irregularity of the bonding, the conformation of the calix[4]arene maintains its cone shape; indeed it is more regular than in any of the other three compounds. The four

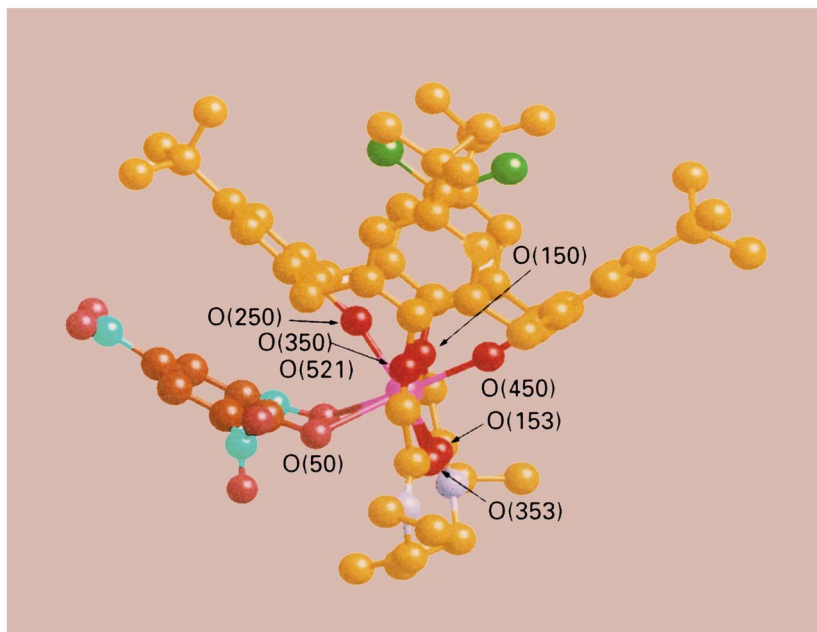


Fig. 1 Structure of $[Tm(LH_{-2})A]$ **1** showing the atomic numbering scheme. A dichloromethane solvent molecule is shown in the cone of the calix[4]arene. Colour key to atoms: metal atoms: magenta; atoms in the calixarene: carbon, yellow; oxygen, red; nitrogen blue; atoms in the picrate: carbon, brown; oxygen, dark red; nitrogen, light blue; atoms in the solvent: methanol oxygen, green; carbon, light brown; water oxygen, green; dichloromethane carbon, yellow; chlorine, green

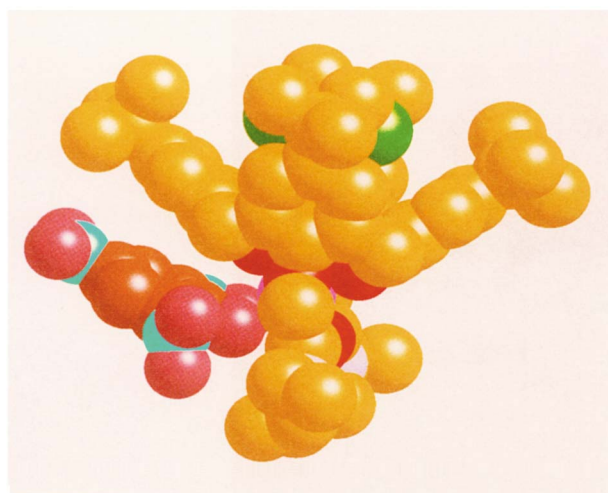


Fig. 2 A space-filling view of $[Tm(LH_{-2})A]$ **1** showing the π -stacking interaction between the picrate anion and one of the phenyl rings in the substituted calix[4]arene. For colour key to atoms see Fig. 1

phenyl rings intersect the plane of the four methylene atoms at angles of 61.4, 54.4, 67.9 and 57.1°. Also as before, the four oxygen atoms O(150), O(250), O(350), O(450) at the bottom of the rim maintain a plane (root mean square deviation 0.06 Å) which is parallel to the methylene plane (angle of intersection 1.6°) despite the fact that the metal is only bonded to one of these atoms. As is apparent from Fig. 6, the metal atom is situated outside the cone cavity so that it is only within bonding distance of O(250). In the previous structures the metal atom was sited between the planes of donor atoms. By contrast, here the metal and two carbonyl oxygen atoms O(153), O(353) form a plane that is close to parallel to the four-oxygen-atom plane (angle of intersection 8.2°). These three donor atoms are all to one side of the metal, with the three chelating picrate ions on the opposite side. These three chelating six-membered rings are significantly non-planar Pr, O(*n*0), O(*n*21) vs. O(*n*0), C(*n*1), C(*n*2), N(*n*20), O(*n*21) give angles of 11.2, 2.5 and 42.9° for *n* =

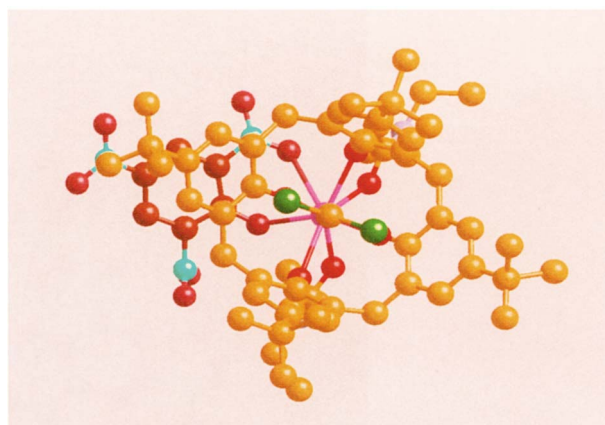


Fig. 3 Structure of $[Tm(LH_{-2})A]$ **1** looking down the cone axis showing the metal co-ordination sphere and the distorted square-antiprismatic geometry. For colour key to atoms see Fig. 1

5, 6 or 7 respectively. The nitro groups in the three picrates are not coplanar with the phenyl ring, making angles of 4.1, 4.9, 7.1; 12.5, 9.7, 71.4 and 26.0, 6.6, 39.8° respectively. It is notable that there is no close contact between the picrate and calixarene phenyl rings, unlike in complexes **1** and **2**, consistent with the observed differences in colour and UV/VIS spectra described above.

The structure of L-2HA is shown in Fig. 7. The calix[4]arene exhibits crystallographic C_2 symmetry. The conformation of the calix[4]arene is more regular than in the metal complexes. Thus the two independent phenyl rings intersect the methylene plane at angles of 52.2 and 66.8° respectively. As is apparent in Fig. 7 (and emphasised in the space-filling picture, Fig. 8), the picric acid ring is approximately parallel to the phenyl ring 2 of the calix[4]arene with an angle of intersection of 8.6°. The closest interaction between atoms in the two rings is 3.29 Å between C(53) and C(21). One of the three nitro groups is disordered. The angles between the other two nitro groups and the picric acid ring are 4.9 and 10.5° respectively. In this

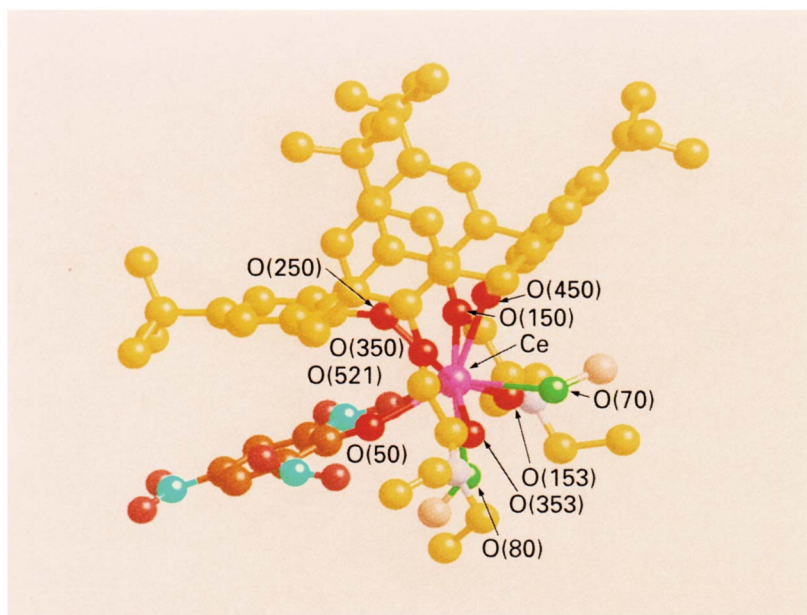


Fig. 4 Structure of $[\text{Ce}(\text{LH}_{-2})(\text{MeOH})_2\text{A}] \mathbf{2}$. For colour key to atoms see Fig. 1

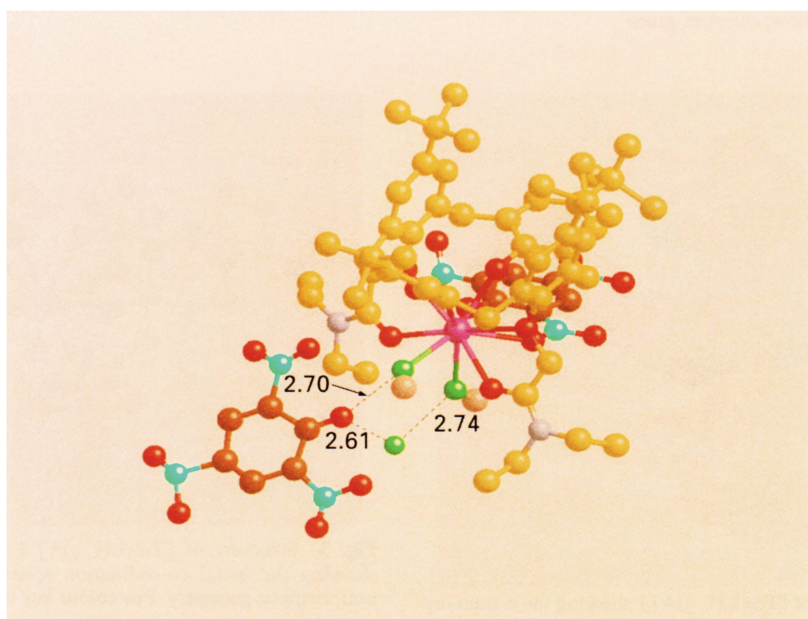


Fig. 5 Structure of $[\text{Ce}(\text{LH}_{-2})(\text{MeOH})_2\text{A}\cdot\text{HA}\cdot\text{H}_2\text{O}] \mathbf{2}$ showing the intermolecular hydrogen bonds. For colour key to atoms see Fig. 1

particular structure, in the absence of the metal atom, the carbonyl groups diverge away from the axis of the calixarene cone.

There are several close contacts indicative of intra- and intermolecular hydrogen bonding. Thus O(250) is within hydrogen-bond distance of both O(150) at 2.80 and O(153) at 2.70 Å suggesting either a bifurcated hydrogen bond or some disorder in the hydrogen position. In addition the nitro oxygen atom O(521) may form an intermolecular hydrogen bond to the carbonyl oxygen atom O(153) at 2.94 Å. There is also the likelihood of an intramolecular hydrogen bond between the phenolic picrate oxygen O(50) and O(521) whose distance is 2.56 Å.

Once again, there are several possibilities for the charge distribution in this structure. One possibility is that both molecules are neutral, in which case there is, of course, no

hydrogen bond between O(521) and O(153). Alternatively, each picrate can lose a proton to be negatively charged which necessitates a dipositive charge for the calix[4]arene moiety, presumably by protonation of the amide oxygen atoms though the C(152)–O(153) distance of 1.239(12) Å is indicative of a double bond. The O atom close contacts described above do not allow us to differentiate between these possibilities, and indeed, it is possible that hydrogen atom positions are disordered in the structure.

The results of these synthetic and structural studies may be summarised as follows. The calix[4]arene diamide (L) combines with lanthanide(III) picrates, in the presence of base, to produce a series of complexes that can be formulated as $[\text{Ln}(\text{LH}_{-2})\text{A}]$. In the absence of base, the complexes generally isolated can be formulated as $[\text{LnLA}_3]$ (at least for La, Ce, Pr and Eu). The most significant variation in this system, across

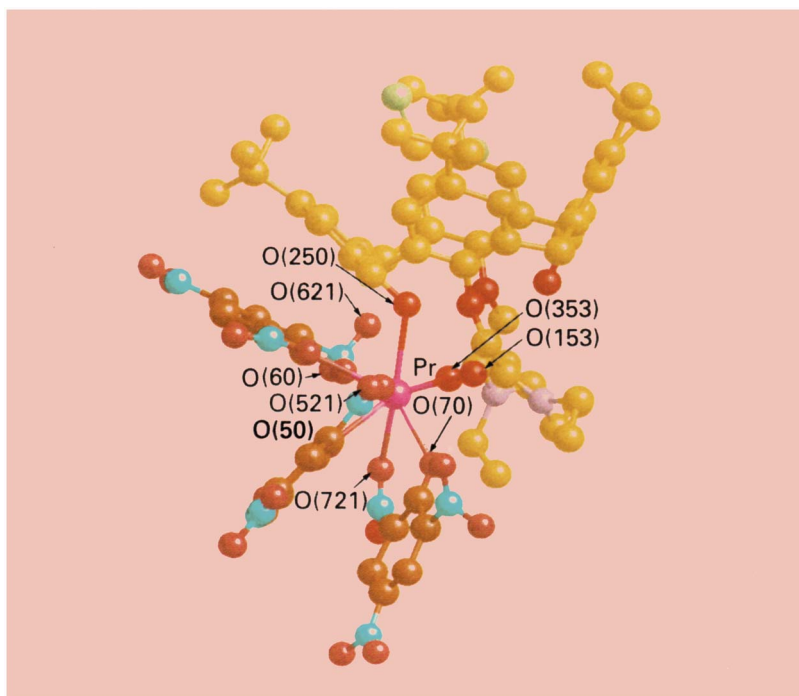


Fig. 6 Structure of $[\text{PrLA}_3] \mathbf{3}$ showing the atomic numbering scheme. For colour key to atoms see Fig. 1

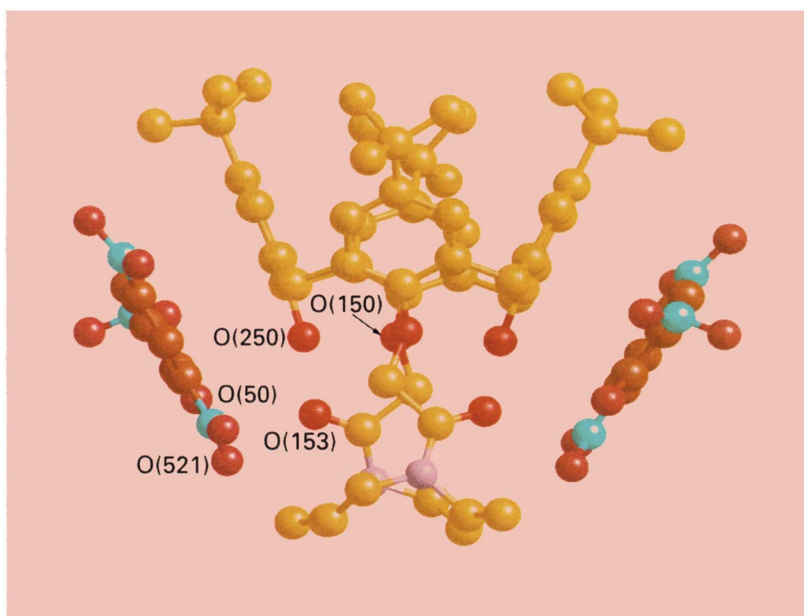


Fig. 7 Structure of $\text{L} \cdot 2\text{HA} \mathbf{4}$ showing the atomic numbering scheme. For colour key to atoms see Fig. 1

the lanthanide series, is found upon recrystallisation of the latter complexes from a dichloromethane-methanol mixture. While the complexes of the heavier lanthanides are recovered unchanged (at least for Pr and Eu), the lanthanum and cerium complexes undergo a reaction to give $[\text{Ln}(\text{LH}_2)(\text{MeOH})_2\text{A}] \cdot \text{HA}$; this change in the chemistry is presumably induced by the larger size of the La^{III} and Ce^{III} cations. Interaction between the phenyl ring of a picrate anion, and a calixarene phenyl ring are observed in a number of these complexes. The relevance of such interactions to the formation and stability of the complexes is not fully apparent but the isolation of the picric acid adduct of L suggests that they may be significant in at least some cases.

It is apparent from the structures described here, that the disposition of a picrate phenyl ring close to a calixarene phenyl ring, gives rise to an intensely coloured complex, presumably due to a charge-transfer absorbance. While the solution chemistry of these systems requires more detailed investigation, it appears from UV/VIS spectroscopy, that at least some features of the solid-state structures are maintained in dichloromethane solution. The importance of this structural feature in processes such as metal-ion extraction in the presence of picrate is yet to be established. The remarkable differences observed in the chemistry of the light lanthanide systems, at least in the absence of base, suggest that the calixarene L, may exhibit some selectivity in the binding of lanthanide cations.

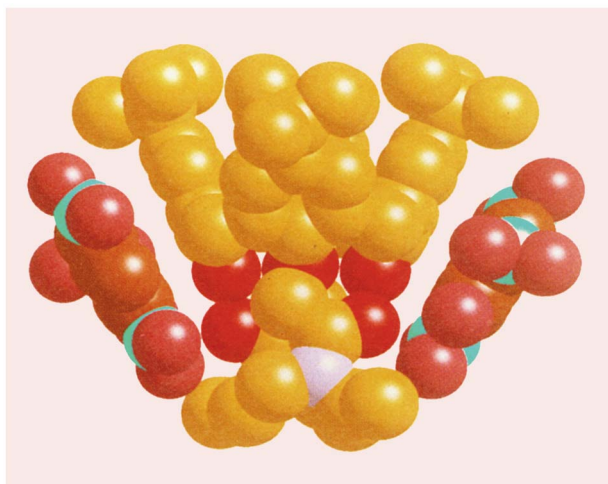


Fig. 8 A space-filling picture of L-2HA **4** showing the π -stacking interaction between the picric acid and the substituted calix[4]arene. For colour key to atoms see Fig. 1

This possibility, with particular emphasis on the extraction of lanthanides from aqueous solution, is currently under investigation.²¹

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