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Lanthanide Structures, Coordination, and Extraction Investigations of a 1,3-Bis(diethyl amide)-Substituted Calix[4]arene Ligand

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The synthesis and structure determinations of lanthanum, samarium, ytterbium, and lutetium complexes of 5,11,17,23-tetra-*tert*-butyl-25,27-bis((diethylcarbamoyl)methoxy)-26,28-dihydroxycalix[4]arene (**L**) are described. The four structures display similar characteristics with the trivalent lanthanide cation being encapsulated in an eight-coordinate oxygen environment, consisting of six oxygens from the calixarene, a water molecule, and unidentate picrate for lanthanum [La(**L**-2H)(picrate)(H_2O)]; and bidentate chelating picrate for the other lanthanides [Ln(**L**-2H)(picrate)]Ln = Sm, Yb, Lu. Under optimised experimental conditions solvent extraction investigations showed the calix[4]arene ligand **L** exhibited generally very high percentage extractabilities of lanthanide cations into dichloromethane, presumably on account of the ligand's unique lower rim oxygen containing coordination sphere and its lipophilic exterior.

Introduction

The calix[4]arene macrocyclic structural framework[1,2] has been shown to be an attractive building block which can be selectively functionalized both at the hydroxyl lower rim[3] and at the upper rim[4] para positions of the phenol aryl moieties for the coordination of neutral,[1] cationic[2] and, more recently, anionic guest species.[5] Focussing on metal cations for example, additional donor groups such as esters,[2,6] amides,[2,6] carboxylic acids,[2,7] crown ethers,[8] and spherands[9] have been appended to the lower rim for the complexation of alkali and alkaline earth metal cations, whereas pendent phosphino-,[10] bipyridyl-,[11] and thioether-[2,3] substituted calix[4]arenes have been shown to coordinate transition metals.

In spite of this variety of, in particular, hard donor group substituted calix[4]arene based ligands there have been relatively few reports detailing their potential to coordinate the trivalent lanthanide cations. The coordination properties of the *parent* calixarenes towards the lanthanides have been investigated in detail by most notably Harrowfield and co-workers.[12] Sparse instances with modified calixarenes can be found with lower rim tetrasubstituted calix[4]arenes containing tertiary amide groups,[13] 2,2-bipyridyls,[14] and mixed lower rim trisubstituted carboxylic acids−mono amide calix[4]arenes[15] which encapsulate and shield lanthanide ions from solvent molecules. None of these latter reports however describe any solid state lanthanide−calixarene structural investigations or extraction studies.

Extraction studies of lanthanides have been reviewed recently,[16] and work covering a range of macrocycles is described including calixarenes. However it is reported that while the few results obtained so far indicate a generally high stability for complexes with lanthanides, data are still scarce but a great number of possible derivatives have not yet been tested.

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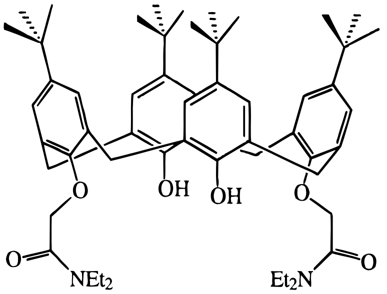
Table 1. Crystal Data and Structure Refinement for **1**−**4**

	1	**2**	**3**	**4**
formula	[La(**L**-2H)(picrate)H_2O)]·3MeCN·CH_2Cl_2	[Sm(**L**-2H)(picrate)], EtOH	[Yb(**L**-2H)(picrate)]·3CH_2Cl_2	[Lu(**L**-2H)(picrate)]·CH_2Cl_2·EtOH·H_2O
empirical formula	$C_{69}H_{91}Cl_2N_8O_{14}La$	$C_{64}H_{84}N_5O_{14}Sm$	$C_{65}H_{86}Cl_6N_5O_{14}Yb$	$C_{65}H_{90}Cl_2N_5O_{15}Lu$
fw	1466.31	1265.14	1547.13	1427.27
T (*K*)	293(2)	293(2) K	293(2)	293(2)
wavelength (Å)	0.71070	0.71070 A	0.71070	0.71070
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	*C*2/c	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell dimens (Å)				
a (Å)	12.631(8)	30.459(8)	13.949(7)	14.147(7)
b (Å)	17.464(9)	12.702(6)	14.876(7)	15.040(7)
c (Å)	17.881(8)	40.757(12)	18.020(7)	18.524(7)
α (deg)	76.61(1)	(90)	87.56(1)	89.08(1)
β (deg)	85.16(1)	112.00(1)	80.97(1)	81.13(1)
γ (deg)	72.77(1)	(90)	72.16(1)	72.32(1)
V ($Å^3$)	3664.3	14620(9)	3515(3)	3708.3
Z	2	8	2	2
D (calcd) (Mg/m^3)	1.329	1.150	1.431	1.276
abs coeff (mm^{-1})	0.720	0.860	1.603	1.464
F(000)	1528	5416	1546	1473
cryst size (mm)	0.35 * 0.35 * 0.20	0.35 * 0.30 * 0.25	0.3 * 0.3 * 0.3	0.3 * 0.3 * 0.3
θ range for data collcn (deg)	2.86−24.99	2.56−25.07	1.78−25.15	2.79−24.88
index ranges	$0 \le h \le 14$	$0 \le h \le 36$	$0 \le h \le 16$	$0 \le h \le 16$
	$-19 \le k \le 20$	$-13 \le k \le 13$	$-16 \le k \le 17$	$-16 \le k \le 17$
	$-20 \le l \le 20$	$-48 \le l \le 44$	$-21 \le l \le 21$	$-21 \le l \le 21$
no. of indep reflcns	9936	19109	11298	11564
data/params	9936/809	11220/744 [R(int) = 0.0453]	11298/795	11564/63/786
goodness-of-fit on F^2	0.574	0.950	0.687	1.127
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0743, wR2 = 0.1675	R1 = 0.0869, wR2 = 0.219	R1 = 0.0849, wR2 = 0.2436	R1 = 0.0932, wR2 = 0.1930
R indices (all data)	R1 = 0.1160, wR2 = 0.3686	R1 = 0.1234, wR2 = 0.2702	R1 = 0.1406, wR2 = 0.3086	R1 = 0.1222, wR2 = 0.2072
largest diff peak and hole (e $Å^{-3}$)	1.542 and -1.287	1.851 and −0.761	2.276 and −2.449	1.417 and −1.989

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|]$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2)/\sum[w(F_o^2)^2]^{1/2}$.

We report here one such study describing the synthesis and structure determinations of lanthanum, samarium, ytterbium, and lutetium complexes of a 1,3-bis(diethyl amide)-substituted calix[4]arene ligand **L** and in addition this ligand's noteworthy lanthanide solvent extraction capabilities.



L

Experimental Section

Synthesis. 5,11,17,23-Tetra-*tert*-butyl-25,27-bis((diethylcarbamoyl)methoxy)-26,28-dihydroxycalix[4]arene[3] (**L**), and the lanthanide picrate dodecahydrates[17] were synthesised by literature methods. Lanthanide analyses were performed on a ThermoElectron AtomScan 25 sequential ICP-AES.

Synthesis of Ln(L-2H)(picrate)·*x*H_2O. A solution of Ln(picrate)$_3$.12H_2O (0.025 mmol) in ethanol (1.5 mL) was added to a solution of the calixarene **L** (0.023 mmol) in dichloromethane (1.5 mL). Triethylamine (0.02 mL) was then added, to give a dark brown solution, which was filtered and left to evaporate. The product usually precipitated as large dark brown rhombs, with occasional formation of fine needles (presumably due to subtle changes in the reaction conditions). Microanalytical results suggested that the composition of the product is the same in each case, but the fine needles were not appropriate for crystallographic studies, and hence the product was recrystallized from dichloromethane/ethanol to form the larger crystals when necessary. For X-ray diffraction studies, crystals were kept wet with supernatant solution. Crystals collected in the laboratory atmosphere, washed with ethanol, and dried by vacuum desiccation became opaque. Microanalyses were consistent with loss of solvent relative to the stoichiometries implied by the structure determinations.

Microanalysis. (**1**) [La(**L**-2H)(picrate)(H_2O)]·H_2O, (Found: C, 58.5; H, 6.28; N, 5.48. Calcd for $C_{62}H_{82}LaN_5O_{15}$: C, 58.4; H, 6.48; N. 5.49.)

(**2**) [Sm(**L**-2H)(picrate)] (Found: C, 59.4; H, 6.33; N, 5.52. Calcd for $C_{62}H_{78}N_5O_{13}Sm$: C, 59.5; H, 6.28; N, 5.59).

(**3**) [Yb(**L**-2H)(picrate)]·H_2O (Found: C, 57.7; H, 5.97; N, 5.24. Calcd for $C_{62}H_{80}N_5O_{14}Yb$: C, 57.6; H, 6.24; N. 5.42).

(**4**) [Lu(**L**-2H)(picrate) (Found: C, 58.1; H, 6.15; N, 5.51. Calcd for $C_{62}H_{78}LuN_5O_{13}$: C, 58.3; H, 6.16; N. 5.49).

X-ray Crystallography. Crystals were prepared as described above and loaded in thin-walled capillaries. Crystals were found to decompose 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 [La(**L**-2H)(picrate)(H_2O)]·3MeCN. CH_2Cl_2 (**1**), [Sm(**L**-2H)(picrate)]·EtOH (**2**), [Yb(**L**-2H)(picrate)]·3CH_2Cl_2·H_2O (**3**), [Lu(**L**-2H)(picrate)]·CH_2Cl_2·EtOH·2H_2O (**4**) were collected with Mo Kα radiation using the MARresearch image plate system. The crystals were positioned at 75 mm from the image plate. A total of 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out

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Table 2. Atomic coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**[a]

	x	*y*	*z*	U(eq)[a]		*x*	*y*	*z*	U(eq)[a]
La	1447(1)	2889(1)	3463(1)	53(1)	C(358)	−2612(23)	2528(18)	5478(24)	141(14)
C(11)	1632(14)	3958(10)	1030(9)	48(4)	O(450)	482(10)	2989(7)	2445(7)	57(3)
C(12)	1954(12)	3859(11)	284(10)	56(4)	C(100)	3397(17)	3445(13)	−767(11)	73(5)
C(13)	2977(16)	3515(12)	124(11)	66(5)	C(101)	4067(23)	4025(16)	−1045(15)	101(8)
C(14)	3787(15)	3150(11)	652(10)	60(5)	C(102)	2355(19)	3703(17)	−1264(12)	91(7)
C(15)	3502(15)	3256(11)	1410(11)	58(4)	C(103)	4024(24)	2592(15)	−815(14)	108(9)
C(16)	2455(17)	3707(11)	1560(10)	64(5)	C(200)	6430(20)	7(13)	1582(16)	101(10)
C(17)	4392(13)	2820(11)	2044(11)	57(4)	C(201)	7244(25)	386(23)	1171(26)	171(19)
C(21)	4535(12)	1907(9)	2240(8)	43(3)	C(202)	5883(45)	18(49)	849(37)	302(45)
C(22)	5343(14)	1426(10)	1836(13)	66(5)	C(203)	6827(56)	−765(25)	1985(28)	397(66)
C(23)	5512(15)	555(12)	1998(12)	70(5)	C(300)	1592(16)	−636(12)	1568(11)	69(5)
C(24)	4789(16)	275(12)	2544(12)	67(5)	C(301)	1665(32)	−1474(14)	2027(15)	132(13)
C(25)	3988(13)	738(12)	2924(10)	56(4)	C(302)	2600(23)	−664(16)	1072(16)	101(8)
C(26)	3871(12)	1577(10)	2751(10)	50(4)	C(303)	689(26)	−380(23)	1037(24)	199(25)
C(27)	3224(12)	361(10)	3479(10)	52(4)	C(400)	−2209(20)	3350(13)	−48(10)	78(7)
C(31)	2211(11)	397(8)	3049(10)	45(4)	C(401)	−2724(29)	2656(15)	−24(18)	125(12)
C(32)	2286(18)	−84(11)	2557(11)	66(5)	C(402)	−3060(29)	4133(31)	−255(26)	222(27)
C(33)	1378(15)	−23(9)	2095(9)	53(4)	C(403)	−1528(30)	3464(28)	−747(17)	191(22)
C(34)	517(14)	593(9)	2116(11)	53(4)	W(1)	47(14)	4334(9)	3519(11)	104(5)
C(35)	369(14)	1116(10)	2614(10)	55(4)	O(50)	1850(16)	2390(12)	4844(9)	107(6)
C(36)	1219(13)	978(10)	3112(11)	53(4)	C(51)	2451(21)	2494(20)	5345(12)	102(10)
C(37)	−688(13)	1828(9)	2584(10)	51(4)	C(52)	3516(19)	1860(14)	5639(12)	76(6)
C(41)	−771(13)	2515(9)	1912(10)	50(4)	C(53)	4166(20)	1962(13)	6079(10)	74(6)
C(42)	−1401(14)	2607(11)	1253(11)	63(5)	C(54)	3911(15)	2671(15)	6369(11)	71(6)
C(43)	−1521(14)	3246(11)	658(11)	58(4)	C(55)	2951(18)	3252(14)	6182(11)	75(6)
C(44)	−941(13)	3806(11)	651(11)	56(4)	C(56)	2316(21)	3155(13)	5699(12)	84(7)
C(45)	−257(12)	3722(9)	1230(12)	56(5)	N(520)	3759(21)	1071(17)	5381(14)	107(7)
C(46)	−143(12)	3073(11)	1868(10)	55(4)	O(521)	3079(23)	745(14)	5333(16)	145(8)
C(47)	421(14)	4326(11)	1215(12)	63(5)	O(522)	4701(28)	906(17)	5097(22)	204(14)
O(150)	2206(10)	3841(6)	2316(7)	55(3)	N(540)	4654(19)	2755(15)	6873(15)	104(7)
C(151)	2644(15)	4482(10)	2444(11)	63(5)	O(541)	5460(19)	2181(16)	7092(14)	145(9)
C(152)	2824(16)	4334(12)	3254(12)	66(5)	O(542)	4469(23)	3365(18)	7083(16)	159(10)
O(153)	2571(13)	3799(9)	3725(8)	78(4)	N(560)	1197(27)	3748(17)	5513(19)	143(11)
N(154)	3357(15)	4815(11)	3463(10)	77(5)	O(561)	464(24)	3635(18)	5333(35)	340(35)
C(155)	3806(27)	5439(15)	2951(15)	102(8)	O(562)	1238(24)	4456(15)	5606(13)	154(10)
C(156)	2864(33)	6286(19)	2833(19)	142(14)	N(700)	1916(24)	−819(17)	5489(17)	132(9)
C(157)	3486(26)	4721(15)	4325(15)	102(8)	C(701)	2619(28)	−1014(19)	5861(19)	114(9)
C(158)	4599(36)	4114(33)	4590(24)	215(24)	C(702)	3721(32)	−1341(25)	6238(23)	163(14)
O(250)	3060(9)	2077(7)	3109(8)	65(3)	C(800)	7683(28)	3949(21)	2933(21)	131(11)
O(350)	1039(9)	1482(7)	3649(7)	54(3)	Cl(01)	7190(18)	4621(14)	3442(12)	280(9)
C(351)	516(16)	1189(11)	4347(11)	65(5)	Cl(02)	6593(19)	3502(14)	2851(12)	297(10)
C(352)	−111(12)	1899(10)	4668(9)	45(4)	N(900)	−113(30)	5919(24)	2618(21)	172(13)
O(353)	−282(12)	2614(8)	4228(8)	73(4)	C(901)	−346(24)	6570(20)	2417(17)	107(8)
N(354)	−602(13)	1802(9)	5326(9)	63(4)	C(902)	−669(30)	7417(22)	2191(21)	140(12)
C(355)	−335(19)	1008(12)	5862(12)	73(5)	N(903)	2262(22)	1721(17)	1118(16)	121(8)
C(356)	551(27)	863(16)	6404(15)	111(10)	C(904)	1672(28)	1781(20)	406(22)	122(10)
C(357)	−1347(22)	2522(14)	5595(16)	104(9)	C(905)	1417(28)	1776(20)	−96(20)	121(10)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

with the XDS program.[18] The positions of the heavy atoms in **1**, **2**, and **4** were determined using direct methods with the Shelx86 program[19] and the remaining atoms were located via Fourier methods. **3** (M = Yb) was found to be isomorphous with **4** (M = Lu), and input coordinates were therefore taken from the refined structure of **4**. All structures exhibited features of disorder, particularly in the *tert*-butyl groups at the top of the calix[4]arene cavity and in addition showed a variety of solvent molecules. All ordered non-hydrogen atoms in the complexes were refined with anisotropic thermal parameters. When the *tert*-butyl groups were disordered, which was often, two sets of constrained tetrahedra were refined with occupancies that added up to 1.0. High thermal parameters were obtained for the amide ethyl groups at the bottom of the cone and for some nitro groups. Disordered models were tried but with few exceptions they did not give any significantly better fits. Solvent molecules, of which there were many, were included with isotropic thermal parameters. Hydrogen atoms were included in geometric positions (methyls as rigid groups) with thermal parameters equivalent to 1.2 times the atom to which they were bonded. The structures were then refined using Shelxl.[20] Neither absorption nor extinction corrections were carried out. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Atomic coordinates in the four structures are given in Table 2−5 inclusive. Dimensions in the metal coordination spheres are compared in Table 6. Data for three similar compounds with different lanthanides were also measured. M = Er, Tm were found to be isomorphous with **3** and **4** and M = Pr with **2** but structural details are not reported here.[25]

Extraction Experiments. Standard lanthanide solutions were made from high purity lanthanide carbonates (99.99%) dissolved in nitric acid. Picric acid was introduced to obtain stock source phase solutions containing 0.4 mM lanthanide and 9.6 mM picrate. The aqueous solution was altered to the required pH with lithium hydroxide solution. The pH was maintained at 5.8 ± 0.3 in these experiments. The extractant solvent phase was produced by dissolving the calixarene **L** in dichloromethane to a concentration of 9.6 mM. Thus, the ratio of lanthanide:picrate:**L** was 1:25:25.

Equal volumes (10 mL) of each solution were mixed in a sealed flask, and stirred rapidly for 1 h at 22 °C, after which the mixture was transferred to a separating flask and allowed to settle for 3 h. The aqueous layer was removed and the lanthanide concentration determined.

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(19) Shelx86. Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(20) Sheldrick, G. M. Shelxl. Package for crystal structure refinement, University of Gottingen, 1993.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**

	x	*y*	*z*	*U*(eq)[b]		*x*	*y*	*z*	*U*(eq)[b]
Sm(1)	2729(1)	3121(1)	1607(1)	37(1)	C(400)	649(4)	7134(10)	984(4)	70(3)
C(11)	2173(3)	5129(7)	743(2)	35(2)	C(401)	272(7)	6917(17)	1121(7)	164(11)
C(12)	1794(3)	5220(7)	434(2)	42(2)	C(402)	419(10)	6970(29)	609(6)	266(23)
C(13)	1683(4)	4454(9)	174(2)	49(3)	C(403)	773(8)	8190(15)	1076(11)	264(22)
C(14)	1973(4)	3615(8)	228(2)	46(2)	O(250)	2442(2)	2110(5)	1166(2)	46(2)
C(15)	2372(3)	3493(7)	533(2)	38(2)	O(450)	2196(2)	4327(5)	1492(2)	38(1)
C(16)	2461(3)	4253(7)	784(2)	33(2)	O(150)	2841(2)	4122(4)	1108(1)	36(1)
C(17)	2673(3)	2505(7)	579(2)	40(2)	C(151)	3259(3)	4621(7)	1141(2)	39(2)
C(21)	2406(3)	1551(7)	608(2)	36(2)	C(152)	3557(3)	4656(8)	1530(3)	44(2)
C(22)	2264(3)	811(7)	345(2)	44(2)	O(153)	3375(2)	4380(5)	1744(2)	45(2)
C(23)	1981(4)	−84(8)	354(3)	52(3)	N(154)	4006(3)	4961(8)	1630(3)	66(3)
C(24)	1880(4)	−179(7)	659(2)	48(2)	C(155)	4290(6)	5063(19)	2003(5)	127(7)
C(25)	2029(3)	554(7)	934(2)	41(2)	C(156)[a]	4266(15)	6182(23)	2136(11)	131(14)
C(26)	2293(4)	1415(7)	911(2)	44(2)	C(159)[a]	4432(20)	4020(44)	2133(15)	190(22)
C(27)	1894(4)	451(7)	1246(2)	45(2)	C(157)	4227(5)	5230(11)	1372(4)	81(4)
C(31)	1529(3)	1276(8)	1239(2)	42(2)	C(158)	4462(6)	4323(15)	1275(6)	127(7)
C(32)	1086(4)	1220(8)	985(3)	51(3)	O(350)	2080(2)	2196(5)	1732(2)	41(2)
C(33)	741(4)	1984(10)	949(3)	65(3)	C(351)	2131(3)	1816(8)	2068(2)	46(2)
C(34)	867(3)	2797(8)	1182(3)	50(2)	C(352)	2577(4)	2289(9)	2318(2)	52(3)
C(35)	1303(3)	2906(7)	1443(2)	42(2)	O(353)	2779(2)	3008(5)	2216(2)	45(2)
C(36)	1625(3)	2109(7)	1474(2)	38(2)	N(354)	2754(3)	1926(8)	2646(2)	61(2)
C(37)	1417(4)	3870(8)	1669(2)	46(2)	C(355)	3194(5)	2346(15)	2892(3)	94(5)
C(41)	1441(3)	4826(7)	1468(2)	38(2)	C(356)	3613(8)	1873(29)	2826(6)	95(11)
C(42)	1065(3)	5538(8)	1342(2)	47(2)	C(357)	2541(5)	1055(10)	2771(3)	67(3)
C(43)	1066(4)	6385(8)	1133(2)	47(2)	C(358)	2229(6)	1458(13)	2953(4)	96(5)
C(44)	1465(4)	6513(8)	1052(3)	48(2)	C(51)	3224(6)	690(10)	1748(3)	85(4)
C(45)	1849(3)	5844(7)	1167(2)	35(2)	C(52)	3422(5)	679(9)	1476(3)	66(3)
C(46)	1833(3)	4989(7)	1377(2)	35(2)	C(53)	3473(6)	−203(10)	1303(4)	85(4)
C(47)	2232(3)	5920(7)	1030(2)	37(2)	C(54)	3361(7)	−1146(11)	1398(5)	111(6)
C(100)	1247(4)	4583(10)	−160(3)	65(3)	C(55)	3201(6)	−1246(12)	1675(5)	108(6)
C(101)	1350(8)	5324(22)	−392(5)	210(15)	C(56)	3156(7)	−331(12)	1837(5)	108(6)
C(102)	1118(7)	3611(17)	−375(5)	166(11)	O(50)	3130(3)	1474(6)	1881(2)	73(2)
C(103)	845(7)	4946(23)	−82(5)	189(13)	N(520)	3594(4)	1634(8)	1383(3)	72(3)
C(200)	1822(4)	−832(9)	74(3)	77(4)	O(521)	3490(3)	2479(6)	1474(2)	69(2)
C(201)[a]	2198(10)	−1164(27)	−73(9)	103(10)	O(522)	3844(5)	1607(8)	1202(3)	124(5)
C(202)[a]	1458(9)	−1636(19)	101(7)	77(7)	N(540)	3407(8)	−2103(16)	1209(6)	158(7)
C(203)[a]	1493(10)	−254(23)	−263(6)	93(9)	O(541)	3363(7)	−2900(16)	1353(5)	187(7)
C(204)[a]	1981(11)	−1924(13)	216(7)	107(11)	O(542)	3584(7)	−2053(14)	1008(5)	192(7)
C(205)[a]	1986(10)	−692(22)	−224(5)	86(8)	N(560)	2970(8)	−456(18)	2134(5)	140(6)
C(206)[a]	1295(5)	−966(28)	−78(8)	140(14)	O(561)[a]	3174(9)	−20(24)	2374(7)	133(9)
C(300)	252(5)	1920(11)	663(4)	88(5)	O(562)[a]	2597(10)	−846(24)	2027(7)	138(9)
C(301)[a]	193(12)	2851(24)	424(8)	87(9)	O(563)[a]	3225(12)	−898(31)	2381(10)	188(14)
C(302)[a]	104(12)	877(26)	521(9)	99(10)	O(564)[a]	2628(20)	−71(62)	2111(18)	387(42)
C(303)[a]	−146(15)	2205(37)	820(11)	133(14)	C(500)	4039(19)	5104(43)	3022(14)	176(21)
C(304)[a]	272(14)	1276(32)	347(10)	120(12)	C(501)	4213(17)	5754(41)	3124(13)	144(16)
C(305)[a]	−23(15)	1130(38)	801(12)	144(15)	O(502)	4165(15)	6695(35)	2904(12)	214(17)
C(306)[a]	−4(15)	2851(32)	547(12)	122(13)					

[a] Occupation factor of 0.50. [b] See footnote *a* in Table 2.

Results and Discussion

The lanthanum, samarium, ytterbium, and lutetium complexes of **L** were prepared via the addition of the respective lanthanide picrate dodecahydrate[17] in ethanol to a dichloromethane solution of the calixarene **L**[3] in the presence of triethylamine. Slow evaporation of the solvent led to the precipitation of the lanthanide complexes whose microanalytical results suggested the general formulation [Ln(**L**-2H) (picrate)]$\cdot x$H$_2$O. (See Experimental Section.) Crystals suitable for X-ray structural determinations were grown from dichloromethane/ethanol solvent mixtures. The four structures all contain discrete molecules of the metal complexed with calix[4]arenediamide together with solvent molecules. The common numbering scheme is shown in Charts 1 and 2.

The metal complexes in structures **1**−**4** are illustrated in Figures 1−4 together with the common numbering system. The structures have very similar features showing an eight-coordinate lanthanide encapsulated within the calix[4]arenediamide which has the cone conformation. In this conformation the six oxygen atoms in the lower rim, two from the anionic O$^-$ moities O(250) and O(450), two from the ethereal oxygen atoms O(150) and O(350) and two from the amide oxygen atoms O(153), O(353) are all available for bond formation. These six oxygen atoms can bind smaller transition metal ions and indeed the structure of [Fe(**L**-2H)]$^+$ has been determined.[21] Here the metal is six-coordinate with Fe(III)−O bonds ranging from 1.89−2.21 Å. However the metal is in an ideal trigonal prismatic environment with the four oxygen atoms O(150), O(250), O(350), and O(450) forming a rectangular plane and atoms O(153) and O(353) the remaining edge. Our molecular mechanics calculations[21] show that this donor set cannot provide an octahedral environment as is favored by the majority of transition metals because these four oxygen atoms at the lower rim of the substituted calix[4]-arene {O(n50), (n = 1,4)} are perforce nearly planar, and this clearly prevents formation of complexes with these metals.

As shown by the present structures, it is possible to expand the donor set to 8 and provide a suitable environment for the larger lanthanide metals. In the case of La (**1**), the extra donor atoms are a water molecule and the O$^-$ of a picrate anion but for Sm (**2**), Yb (**3**), and Lu (**4**), these extra atoms are provided

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**

	x	*y*	*z*	*U*(eq)[b]
Yb(1)	1338(1)	1931(1)	2643(1)	39(1)
C(11)	−112(8)	559(6)	1460(6)	31(2)
C(12)	−1009(8)	520(7)	1253(7)	39(2)
C(13)	−1822(8)	535(8)	1764(7)	44(3)
C(14)	−1747(9)	609(8)	2501(6)	44(3)
C(15)	−868(9)	617(8)	2738(6)	41(3)
C(16)	−38(8)	556(7)	2216(6)	36(2)
C(17)	−845(10)	731(8)	3569(7)	46(3)
C(21)	−1361(8)	1711(8)	3859(6)	42(3)
C(22)	−2240(10)	1925(9)	4367(7)	52(3)
C(23)	−2731(10)	2814(10)	4678(7)	54(3)
C(24)	−2259(10)	3466(9)	4451(7)	56(3)
C(25)	−1387(9)	3319(8)	3964(6)	46(3)
C(26)	−949(9)	2419(8)	3647(6)	42(3)
C(27)	−890(10)	4044(9)	3760(8)	53(3)
C(31)	−963(10)	4393(8)	2975(7)	49(3)
C(32)	−1853(10)	4970(9)	2799(9)	59(4)
C(33)	−1968(10)	5289(8)	2080(9)	56(3)
C(34)	−1148(10)	4944(8)	1529(8)	52(3)
C(35)	−234(9)	4351(7)	1687(8)	46(3)
C(36)	−155(8)	4122(7)	2383(7)	41(3)
C(37)	587(9)	3947(8)	1036(7)	44(3)
C(41)	448(9)	3168(7)	616(7)	41(3)
C(42)	40(10)	3331(8)	−37(7)	44(3)
C(43)	−101(9)	2608(9)	−431(8)	49(3)
C(44)	143(9)	1751(8)	−127(6)	40(2)
C(45)	510(8)	1579(7)	531(6)	35(2)
C(46)	679(8)	2293(7)	920(6)	36(2)
C(47)	763(8)	617(7)	865(6)	36(2)
C(100)	−2775(9)	436(9)	1517(8)	52(3)
C(101)	−3697(11)	993(13)	1975(11)	90(6)
C(102)	−2682(13)	−615(12)	1529(13)	92(6)
C(103)	−2849(15)	705(20)	713(11)	115(8)
C(200)	−3717(13)	3002(12)	5258(10)	79(5)
C(201)	−3718(26)	3628(27)	5807(17)	207(19)
C(202)	−4517(16)	3501(31)	4820(17)	196(19)
C(203)	−3925(38)	2229(20)	5538(28)	321(39)
C(300)	−2958(12)	5990(11)	1907(11)	76(5)
C(301)[a]	−3787(31)	5616(30)	2213(24)	89(11)
C(302)[a]	−3088(48)	6869(41)	2292(35)	139(19)
C(303)[a]	−2970(40)	6160(37)	1144(28)	119(15)
C(304)[a]	−2836(25)	6938(22)	1719(19)	69(8)
C(305)[a]	−3815(33)	6225(32)	2551(25)	100(12)
C(306)[a]	−3475(38)	5541(35)	1435(28)	115(14)
C(400)	−514(11)	2802(10)	−1178(7)	54(3)
C(401)[a]	−744(23)	2026(20)	−1490(16)	59(7)
C(402)[a]	176(26)	3100(25)	−1733(19)	76(9)
C(403)[a]	−1572(28)	3719(24)	−1042(21)	78(9)
C(404)[a]	−864(32)	3714(27)	−1410(23)	91(11)
C(405)[a]	−1442(28)	2470(26)	−1118(21)	84(10)
C(406)[a]	277(27)	2124(25)	−1784(20)	80(9)
O(150)	876(5)	554(5)	2435(4)	37(2)
C(151)	1618(8)	−352(7)	2373(6)	38(2)
C(152)	2625(8)	−165(8)	2278(7)	41(3)
O(153)	2649(5)	634(5)	2309(5)	42(2)
N(154)	3450(8)	−877(7)	2191(7)	58(3)
C(155)	3425(12)	−1849(10)	2120(11)	77(5)
C(156)	3714(15)	−2149(14)	1324(11)	101(7)
C(157)	4420(10)	−715(11)	2152(11)	74(5)
C(158)	4685(17)	−661(17)	2916(13)	116(8)
O(250)	1058(6)	2124(5)	1546(5)	45(2)
O(350)	778(6)	3606(5)	2579(5)	41(2)
C(351)	1462(9)	4116(7)	2623(8)	46(3)
C(352)	2493(9)	3419(8)	2561(6)	40(2)
O(353)	2614(6)	2595(5)	2381(5)	46(2)
N(354)	3262(8)	3665(8)	2706(8)	66(3)
C(355)	3183(13)	4608(11)	2931(13)	89(6)
C(356)	3644(20)	5101(17)	2334(16)	134(9)
C(357)	4253(10)	2942(12)	2663(12)	83(6)
C(358)	4277(18)	2412(15)	3416(11)	113(8)
O(450)	−86(7)	2218(6)	3174(5)	57(2)
C(51)	1200(10)	2389(10)	4412(7)	54(3)
C(52)	823(10)	1670(9)	4711(7)	51(3)
C(53)	145(9)	1757(10)	5363(7)	51(3)
C(54)	−152(11)	2607(11)	5758(7)	58(3)
C(55)	270(14)	3259(11)	5549(8)	75(5)
C(56)	952(12)	3146(10)	4924(8)	63(4)
O(50)	1701(7)	2403(6)	3778(4)	51(2)
N(520)	1190(9)	796(8)	4361(6)	55(3)
O(521)	1602(8)	708(6)	3719(5)	60(2)
O(522)	1057(10)	112(7)	4710(6)	75(3)
N(540)	−912(11)	2729(11)	6397(7)	73(4)
O(541)	−1226(11)	2078(11)	6578(7)	99(4)
O(542)	−1208(10)	3465(10)	6709(6)	99(4)
N(560)	1477(14)	3852(11)	4724(8)	78(4)
O(561)	1039(19)	4586(15)	4507(14)	187(11)
O(562)	2289(17)	3682(14)	4756(17)	189(11)
C(1)	−2078(13)	2920(12)	1981(9)	74(4)
Cl(2)	−3137(5)	3200(4)	2626(3)	108(2)
Cl(3)	−2321(6)	3092(5)	1091(4)	129(2)
C(4)	3287(25)	1978(21)	617(18)	111(9)
Cl(5)	4089(12)	992(11)	250(8)	192(5)
Cl(6)	3784(12)	2859(11)	586(9)	198(5)
C(7)	3551(49)	1327(46)	5454(37)	215(23)
Cl(8)[a]	2516(17)	1371(16)	6268(12)	179(7)
Cl(9)[a]	3497(17)	470(16)	4921(14)	189(8)
Cl(8A)[a]	2935(30)	1926(27)	6108(22)	158(11)
Cl(9A)[a]	3350(38)	313(36)	5632(29)	202(17)
OW1	−4307(25)	4480(24)	−135(19)	258(15)

[a] Population factors 0.50. [b] See footnote *a* in Table 2.

by a picrate anion chelating in a bidentate fashion. This is also true for the isomorphous Er, Tm, and Pr structures. It is likely to be significant that the largest of the metals, La, has the unique structure with a water molecule in the coordination sphere. As a consequence the geometry of the coordination sphere is different from the others. The structures in **2**−**4** are all similar indicating that this arrangement is stable over a wide range of metal sizes from the small Yb to the large Sm and the even larger Pr. Taking into account the range of metals studied and the lanthanide radii,[26] it can be suggested that all lanthanides except for La and possibly Ce will have the bidentate picrate structure.

Dimensions of the coordination spheres in **1**−**4** are compared in Table 6 and the conformations of the molecules are described by least-squares plane calculations in Table 7. All four structures have similar features. It is usual to describe the cone formation of the calix[4]arene with reference to the plane of four methylene carbon atoms C(17), C(27), C(37), and C(47). The angles of intersection with the four phenyl rings are shown in Table 7. In all structures, rings 1 and 3, which have the amide groups substituted at the oxygen atoms at the bottom of the cone, are more nearly perpendicular to the methylene plane than rings 2 and 4 which are unsubstituted. Thus the cone conformation has C_2 symmetry rather than the C_4 symmetry often found for the unsubstituted calix[4]arene. The four oxygen atoms at the bottom of the cone O(150), O(250), O(350), and O(450) which are all bonded to the metal atom form a plane that is approximately parallel to the methylene plane. The other four donor atoms O(153), O(353), O(50), and O(521) (for structure **1**) also form a plane on the other side of the metal which is also approximately parallel to the methylene plane and also the other four oxygen plane. This results in an approximately square antiprismatic donor set for the metal atom. This is apparent from Figure 4, which is a view of **2** down the cone axis. Despite these similarities the structure of **1** is significantly different from those of **2**−**4** and this is illustrated in Figure 5(a,b). The main features of the structure are similar but the position of the picrate is very different and this results

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **4**

	x	*y*	*z*	*U*(eq)
Lu(1)	1355(1)	1931(1)	2650(1)	32(1)
C(11)	−79(7)	538(6)	1487(5)	27(2)
C(12)	−976(7)	499(7)	1287(6)	33(2)
C(13)	−1794(7)	489(7)	1782(6)	35(2)
C(14)	−1708(8)	549(7)	2511(6)	38(2)
C(15)	−843(7)	594(6)	2754(5)	30(2)
C(16)	−15(7)	531(6)	2213(5)	27(2)
C(17)	−827(8)	707(7)	3558(6)	36(2)
C(21)	−1335(7)	1688(7)	3870(6)	35(2)
C(22)	−2214(8)	1906(9)	4372(6)	45(3)
C(23)	−2676(8)	2783(8)	4695(6)	48(3)
C(24)	−2210(9)	3454(8)	4491(7)	50(3)
C(25)	−1343(7)	3281(7)	3987(6)	37(2)
C(26)	−904(7)	2391(7)	3671(6)	34(2)
C(27)	−848(8)	4033(7)	3810(6)	45(3)
C(31)	−931(8)	4386(7)	3039(6)	37(2)
C(32)	−1836(8)	4976(7)	2889(7)	48(3)
C(33)	−1990(8)	5309(7)	2199(8)	53(3)
C(34)	−1179(8)	4959(7)	1633(7)	45(3)
C(35)	−261(7)	4361(7)	1759(6)	37(2)
C(36)	−148(7)	4135(6)	2462(6)	33(2)
C(37)	565(8)	3975(7)	1110(6)	38(2)
C(41)	417(7)	3190(6)	693(6)	32(2)
C(42)	12(8)	3335(7)	57(6)	39(3)
C(43)	−162(7)	2638(7)	−347(6)	37(2)
C(44)	120(7)	1752(7)	−56(6)	34(2)
C(45)	523(6)	1568(6)	587(5)	27(2)
C(46)	667(7)	2294(6)	965(6)	31(2)
C(47)	759(7)	603(6)	891(6)	32(2)
C(100)	−2741(8)	365(8)	1538(6)	50(3)
C(101)	−3667(8)	971(11)	2028(9)	89(6)
C(102)	−2702(12)	−651(9)	1604(11)	101(7)
C(103)	−2811(11)	614(14)	748(7)	98(6)
C(200)	−3650(10)	3003(9)	5247(7)	69(4)
C(201)[a]	−3527(22)	3394(21)	5951(11)	102(5)
C(202)[a]	−4072(21)	2187(17)	5351(16)	102(5)
C(203)[a]	−4451(18)	3781(18)	4890(15)	102(5)
C(204)[a]	−3500(29)	2208(24)	5813(18)	102(5)
C(205)[a]	−4526(20)	3034(32)	4880(20)	102(5)
C(206)[a]	−3815(30)	3915(21)	5671(21)	102(5)
C(300)	−2966(9)	6039(9)	2088(7)	75(4)
C(301)[a]	−2794(23)	6909(16)	1793(18)	105(5)
C(302)[a]	−3416(22)	5593(21)	1500(16)	105(5)
C(303)[a]	−3777(19)	6199(22)	2762(14)	105(5)
C(305)[a]	−3120(20)	6913(12)	2571(16)	105(5)
C(306)[a]	−2921(20)	6320(20)	1289(10)	105(5)
C(304)[a]	−3853(11)	5661(18)	2307(19)	105(5)
C(400)	−599(9)	2822(7)	−1054(6)	51(3)
C(401)[a]	−798(19)	2006(13)	−1352(12)	74(3)
C(402)[a]	108(16)	3179(16)	−1609(11)	74(3)
C(403)[a]	−1590(14)	3667(14)	−884(13)	74(3)
C(404)[a]	−911(25)	3786(15)	−1275(17)	74(3)
C(405)[a]	201(21)	2196(21)	−1676(13)	74(3)
C(406)[a]	−1477(20)	2378(23)	−981(18)	74(3)
O(150)	895(4)	532(4)	2435(4)	28(2)
C(151)	1617(7)	−362(6)	2385(6)	32(2)
C(152)	2624(7)	−179(7)	2336(6)	36(2)
O(153)	2669(5)	624(4)	2344(4)	35(2)
N(154)	3448(6)	−905(6)	2256(6)	48(3)
C(155)	4415(9)	−737(9)	2266(9)	64(4)
C(156)	4616(13)	−605(15)	3009(11)	104(7)
C(157)	3454(8)	−1876(7)	2198(9)	63(4)
C(158)	3751(14)	−2244(13)	1430(12)	110(7)
O(350)	802(4)	3603(4)	2614(4)	32(2)
C(351)	1468(7)	4136(7)	2677(7)	40(3)
C(352)	2512(8)	3397(8)	2598(6)	38(2)
O(353)	2624(5)	2593(4)	2416(4)	35(2)
N(354)	3273(6)	3690(7)	2748(6)	50(3)
C(355)	4253(8)	2973(10)	2713(9)	68(4)
C(356)	4340(13)	2474(14)	3414(10)	103(6)
C(357)	3194(10)	4631(9)	2981(10)	70(4)
C(358)	3583(16)	5158(13)	2424(12)	108(7)
O(250)	−80(5)	2213(5)	3200(4)	43(2)
O(450)	1048(5)	2124(5)	1594(4)	34(2)
C(51)	1242(8)	2377(8)	4409(7)	44(3)
C(52)	849(9)	1673(8)	4713(6)	43(3)
C(53)	196(9)	1774(9)	5365(6)	48(3)
C(54)	−55(9)	2588(9)	5764(6)	50(3)
C(55)	378(11)	3279(10)	5562(8)	66(4)
C(56)	1024(9)	3152(8)	4925(7)	49(3)
O(50)	1722(6)	2384(6)	3781(4)	47(2)
N(520)	1198(8)	757(7)	4356(6)	52(3)
N(540)	−805(9)	2731(9)	6426(6)	67(3)
N(560)	1541(13)	3853(9)	4719(8)	77(4)
O(521)	1625(7)	676(6)	3718(5)	56(2)
O(522)	1054(9)	95(7)	4684(5)	75(3)
O(541)	−1059(9)	3492(8)	6743(6)	92(4)
O(542)	−1144(10)	2103(9)	6622(6)	99(4)
O(561)	1084(16)	4577(13)	4521(10)	158(8)
O(562)	2345(15)	3694(12)	4820(17)	227(14)
C(60)	−2093(11)	2930(9)	2053(10)	77(5)
Cl(61)	−2375(6)	3088(5)	1172(3)	134(2)
Cl(62)	−3110(4)	3172(4)	2703(3)	103(2)
O(601)	3909(26)	2786(24)	538(18)	141(11)
C(602)	3501(40)	2034(35)	479(29)	140(17)
C(603)	4095(28)	978(24)	364(20)	91(10)
OW1	2612(18)	1380(16)	6189(13)	201(9)
OW2	3543(22)	517(20)	4980(15)	245(11)

[a] Population parameters 0.50. [b] See footnote *a* in Table 2.

in distortions elsewhere. For example in **1** the four angles O(450)−La−O(153), O(450)−La−O(353), O(250)−La−O(153), and O(250)−La−O(353) are 130.9(4), 84.0(4), 86.8(5) and 134.0(4)°, respectively, while in **4** they are 93.8(3), 91.9(3), 135.4(3), and 140.5(3)°, respectively (**2** and **3** are similar to (**4**).

However, the bond length distribution is similar in the four structures, taking into account the differences in atomic radii. In this discussion we will quote values for **4** (M = Lu) although all values are given in Table 7. Values for **3** (M = Yb) are very similar but slightly shorter as befits an atomic radii only 0.05 Å less. Values for M = Sm are from 0.04 to 0.17 Å longer and for M = La up to 0.30 Å longer, consistent with the increase in atomic radii. The shortest bonds are to the negatively charged O^- atoms at the bottom of the calix[4]arene rim (Lu−O(250) 2.048(7), 2.066(6) Å). A search of structures in the Cambridge Crystallographic database indicate that these distances are among the shortest lanthanide to oxygen bond lengths known. It is interesting that the C(*n*6)−O(*n*50)−Lu angles are all close to 180° indicating that the excess electron density from the negative charge is located trans to the C−O bond. The next shortest bonds are to the two amide oxygen atoms, Lu−O(153) = 2.266(7), 2.287(7) Å. Here the C(*n*52)−O(*n*53)−Lu angles are ca. 120°. The bonds to the ethereal oxygens at the bottom of the calix[4]arene rim are ca. 0.1 Å longer at Lu−O(150) = 2.439(6) Å, and Lu−O(350) = 2.399(6) Å. The coordination sphere is completed by the picrate ion which is bonded to the metal in a bidentate fashion via the anionic oxygen O(50) at 2.391 (8) and a nitro oxygen O(521) at 2.702 (9) Å. As expected[27] the bond to the O^- ion is significantly shorter than to the nitro oxygen atom.

The arrangement of the picrate anion in **3** (M = Yb) and **4** (M = Sm) is similar. However in **1**, the picrate is bonded via the anionic O^- (La−O(50) = 2.46(2) Å) and the coordination sphere is completed by a water molecule (La−W(1) = 2.636(14) Å).

The geometry of the coordination spheres of **2**−**4** is very similar with all angles within 8°. The stability of this arrangement is striking with similar coordination sphere pertaining

Table 6. Bond Lengths (Å) and Angles (deg) in the Metal Coordination Spheres

	M = La	M = Sm	M = Yb	M = Lu
M−O(250)	2.247(12)	2.114(6)	2.066(8)	2.048(7)
M−O(450)	2.220(11)	2.153(6)	1.991(9)	2.066(6)
M−O(353)	2.585(14)	2.430(6)	2.241(7)	2.287(7)
M−O(153)	2.560(14)	2.434(6)	2.267(8)	2.266(6)
M−O(150)	2.631(11)	2.468(6)	2.388(7)	2.439(7)
M−O(350)	2.600(10)	2.511(6)	2.375(7)	2.399(6)
M−O(50)	2.46(2)	2.529(8)	2.366(7)	2.381(5)
M−O(521)		2.697(9)	2.592(9)	2.702(8)
M−W(1)	2.636(14)			
O(250)−M−O(450)	97.3(5)	102.0(2)	99.6(4)	99.3(3)
O(250)−M−O(153)	86.8(5)	129.5(3)	136.7(3)	135.4(2)
O(450)−M−O(153)	130.9(4)	93.5(2)	90.7(3)	93.8(3)
O(250)−M−O(353)	134.0(4)	132.8(2)	140.7(3)	140.5(3)
O(450)−M−O(353)	84.0(4)	91.0(2)	90.6(3)	91.8(3)
O(153)−M−O(353)	126.3(5)	84.0(2)	80.4(3)	80.7(2)
O(250)−M−O(50)	93.3(6)	81.1(3)	85.2(4)	84.5(3)
O(450)−M−O(50)	151.2(5)	155.1(3)	154.1(3)	155.0(3)
O(153)−M−O(50)	76.2(5)	103.5(3)	103.2(3)	100.7(3)
O(353)−M−O(50)	69.5(5)	70.0(2)	70.8(3)	70.8(3)
O(250)−M−O(350)	77.2(4)	77.3(2)	79.0(3)	79.7(2)
O(450)−M−O(350)	74.4(4)	77.9(2)	79.2(3)	78.8(2)
O(153)−M−O(350)	134.6(4)	153.1(2)	144.3(3)	144.9(2)
O(353)−M−O(350)	58.7(4)	61.2(3)	65.7(3)	65.5(2)
O(50)−M−O(350)	81.9(5)	78.8(3)	76.8(3)	77.6(3)
O(250)−M−O(150)	75.1(4)	76.0(2)	76.1(3)	75.8(2)
O(450)−M−O(150)	74.3(4)	77.6(2)	78.5(3)	79.1(2)
O(153)−M−O(150)	59.6(4)	60.9(2)	64.9(2)	65.1(2)
O(353)−M−O(150)	146.4(4)	151.1(2)	143.2(3)	143.7(2)
O(50)−M−O(150)	134.5(5)	126.7(2)	127.2(3)	125.5(2)
O(350)−M−O(150)	134.6(4)	138.7(2)	143.2(3)	143.6(2)
O(250)−M−O(521)		76.0(3)	79.8(3)	78.8(3)
O(450)−M−O(521)		143.8(3)	143.5(3)	143.4(2)
O(153)−M−O(521)		64.1(2)	67.8(3)	66.0(2)
O(353)−M−O(521)		117.2(3)	113.1(3)	112.9(2)
O(560)−M−O(521)		61.2(3)	62.4(3)	61.5(3)
O(350)−M−O(521)		134.5(2)	135.1(3)	135.2(2)
O(150)−M−O(521)		66.8(2)	65.8(3)	65.0(2)
O(450)−M−W(1)	84.0(5)			
O(250)−M−W(1)	152.8(5)			
O(50)−M−W(1)	98.5(6)			
O(153)−M−W(1)	72.5(6)			
O(353)−M−W(1)	73.2(5)			
O(350)−M−W(1)	128.6(5)			
O(150)−M−W(1)	79.2(5)			

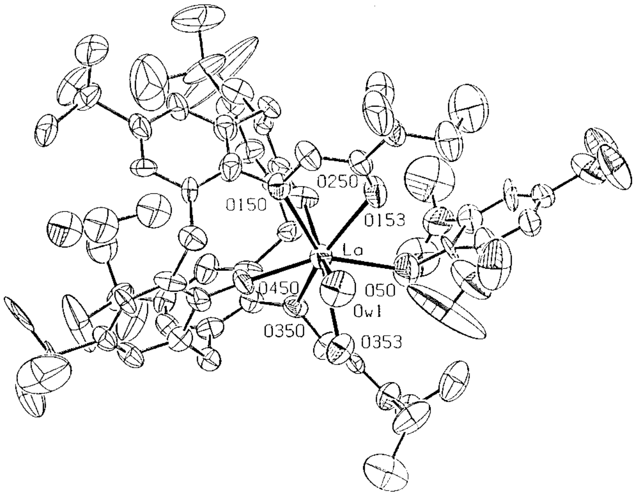

Figure 1. Structure of [La(**L**-2H)(picrate)(H_2O)] (**1**). Thermal ellipsoids are shown at 45% probability. For clarity, the hydrogen atoms not included.

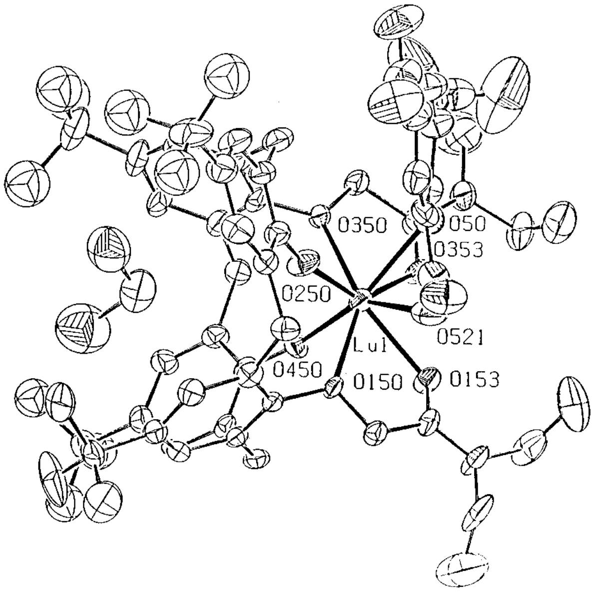

Figure 2. Structure of [Sm(**L**-2H)(picrate)] (**2**). Thermal ellipsoids are shown at 45% probability. For clarity, the hydrogen atoms are not included.

throughout all lanthanides despite variations in atomic radii over a range of 0.3 Å.

It is interesting that in **2**−**4**, the bidentate picrate anion is closely parallel to phenyl ring **2**. This is apparent in Figure 5. The angle of intersection between the planes is ca. 20°. Note the difference in position of the atom O(250) in Figure 4 with reference to the Lu structure compared to the La structure. The position in the Lu structure allows the ring to be more closely parallel in **4**, and this is manifested in the least-squares planes calculations which show that ring 2 is more closely parallel to the methylene plane than ring 4. Rather surprisingly the chelate ring formed by the metal and bidentate picrate is far from planar and the angle between the M, O(50), O(521) plane and the O(50), O(521), C(50), C(51), N(520) plane ranges between 39 and 48° in the three structures. Another feature of interest is that the three nitro groups are all significantly twisted out of the plane of the phenyl ring. The groups on N(520) and N(540) are nearly planar with angles of intersection of ca. 20, and 10° respectively but the group on N(560) is almost perpendicular (angles of intersection 76.2, 69.4, 65.4°). It is noticeable that the nitro group on N(540) is the most planar while that on N(560) is the least planar presumably because it is adjacent to the oxygen O(50) and steric effects are important. However on chelation, the nitro group on N(520) becomes more nearly planar than the other ortho group on N(560). The reasons for the suitability of this system for selective extraction of the lanthanide elements are clear. The calix[4]arenediamide provides a relatively rigid donor set of six oxygen atoms of which two are negatively charged. This feature is suitable for lanthanide elements, but not for transition elements (as the donor set provides a trigonal prismatic and not an octahedral donor set), nor for alkali metals which because of the −2 charge would need to form a negatively charged complex. For the lanthanide elements, the donor set is completed by a picrate anion which provides the third negative charge to balance the Ln^{3+} charge. The coordination number thus becomes 8 which is about average for lanthanides[28] but clearly is a consequence of the rigidity of the calix[4]arene.

All four structures have some solvent in the unit cells. As is usual in the calix[4]arene in the cone conformation, in the majority of structures, one solvent molecule is found in the cone. The other solvent molecules are found filling in the gaps between the molecules in the unit cell. In **1** there are three acetonitrile molecules and one dichloromethane. The acetonitrile is situated within the cavity with the methyl group furthest

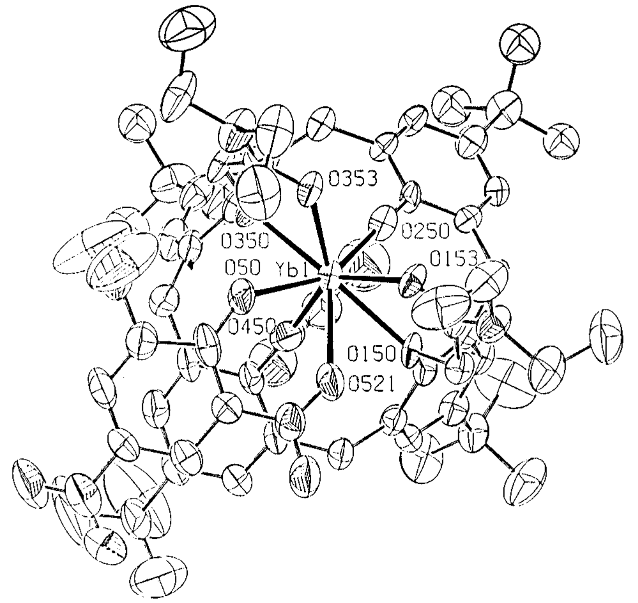

Figure 3. Structure of [Lu(**L**-2H)(picrate)] (**4**). Thermal ellipsoids are shown at 45% probability. For clarity, the hydrogen atoms are not included.

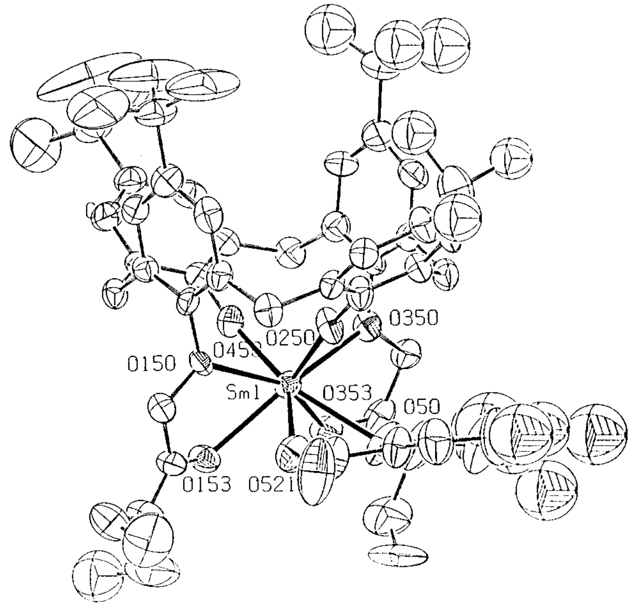

Figure 4. Structure of [Yb(**L**-2H)(picrate)] (**3**) viewed down the calixarene axis. Thermal ellipsoids are shown at 45% probability. For clarity, the hydrogen atoms are not included. The solvent dichloromethane molecule in the cavity is also shown.

in. This arrangement is found in several calix[4]arene structures and is thought to be due to favorable electrostatic interactions between the hydrogen atoms of the methyl group and the phenyl rings. In **3** and **4**, which are isostructural, different solvent molecules are found. In **4**, M = Lu, the solvent consists of one dichloromethane, one ethanol, and two water molecules of which the dichloromethane is found within the cavity. In **3**, M = Yb, there are three dichloromethane molecules and one water molecule of which the dichloromethane is also found within the cavity. In **2**, only one ethanol molecule was located, but this is found within the cavity. The solvent molecule within the cavity is shown in all the figures but the others are excluded.

Lanthanide Extraction Studies. Using the optimised experimental conditions of the calix[4]arene ligand **L** dissolved in dichloromethane (9.6 mM), solvent extractions of aqueous lanthanoid cation solutions (0.4 mM) in the presence of excess picrate (9.6mM) were performed at an aqueous phase pH value of 5.8 ± 0.3. The percentage extractabilities obtained are listed in Table 8. Generally very high percentage extraction was observed for most lanthanide cations, especially with lanthanum (87%), neodymium (98%) europium (89%), and holmium (87%). This contrasts with the percentage extractabilities of lanthanide picrates reported for crown ethers[22,23] and a bis(crown ether)[24] under similar experimental conditions where maximum values of only 20−22% extraction were determined. At low

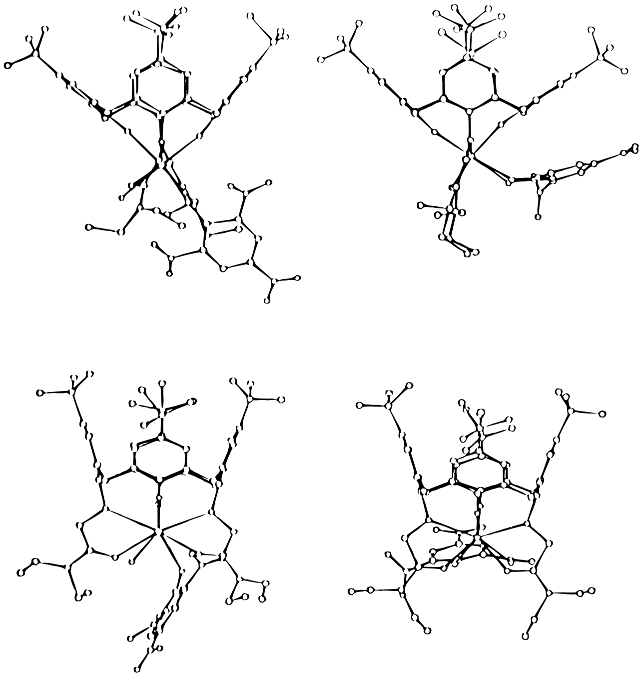

Figure 5. Two views of the structures of **1** (left) and **4** (right) showing the differences between the geometry of the coordination spheres.

Table 7. Least-Squares-Planes Information

plane 1	C(11), C(12), C(13), C(14), C(15), C(16)
plane 2	C(21), C(22), C(23), C(24), C(25), C(26)
plane 3	C(31), C(32), C(33), C(34), C(35), C(36)
plane 4	C(41), C(42), C(43), C(44), C(45), C(46)
plane 5	C(17), C(27), C(37), C(47)
plane 6	O(150), O(250), O(350), O(450)
plane 7	O(153), O(353), O(50), O(521)[a]
plane 8	M, O(50), O(521)
plane 9	O(50), O(521), C(50), C(51), N(520)
plane 10	C(51), C(52), C(53), C(54), C(55), C(56)
plane 11	N(520), O(521), O(522)
plane 12	N(540), O(541), O(542)
plane 13	N(560), O(561), O(562)

Angles between Planes

M	La	Sm	Yb	Lu
1 and 5	73.3	83.8	72.1	71.4
2 and 5	53.1	36.8	33.5	34.0
3 and 5	72.0	81.2	69.6	69.5
4 and 5	41.3	44.1	45.7	46.2
5 and 6	3.5	2.9	4.7	5.3
5 and 7	5.9	3.9	5.2	5.7
6 and 7	2.4	1.6	1.8	1.3
8 and 9		39.0	44.8	47.7
10 and 11	48.1	15.1	20.2	18.7
10 and 12	5.0	15.8	7.9	7.2
10 and 13	24.0	65.4	69.4	76.2
2 and 10		28.5	18.9	20.4

[a] In the case of 1 W(1) replaces O(521) in this plane.

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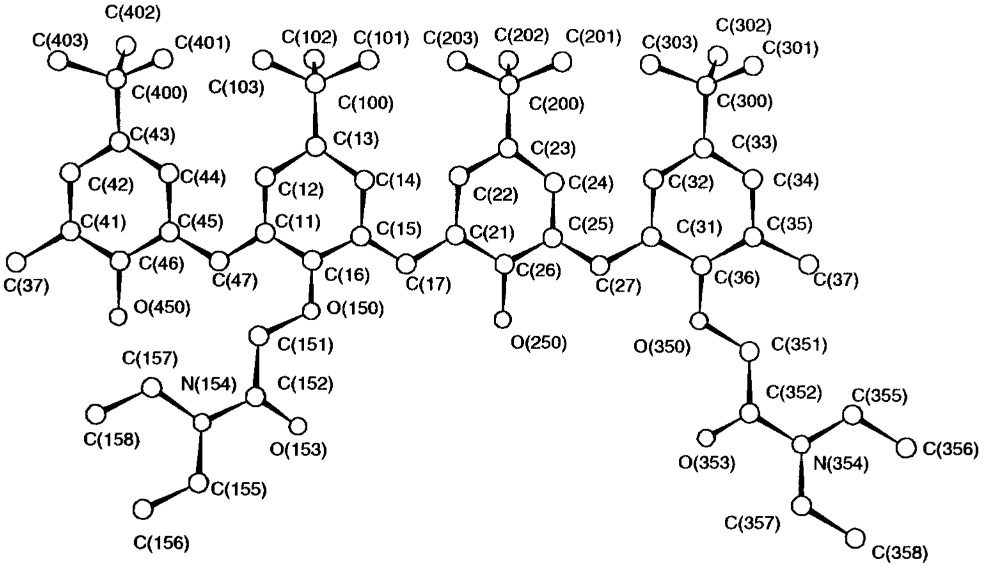
(22) (a) Nakagawa, K.; Okada, S.; Inoue, Y.; Tai, A.; Hakushi, T. *Anal. Chem.* **1988**, *60*, 2527. (b) Nakagawa, K.; Inoue, Y.; Hakushi, T. *J. Chem. Res., Synop.* **1992**, 268; *J. Chem. Res., Miniprint* **1992**, 2122.

Table 8. Solvent Extraction of Lanthanides with **L**[a]

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
extractablity (%)	87	82	83	98	75	89	63	72	71	87	83	84	41	64

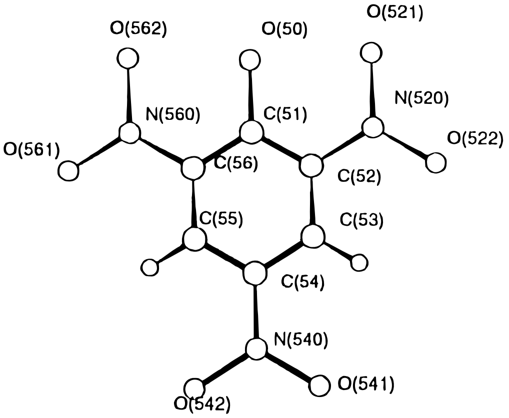
[a] Extraction performed as described in the text.

Chart 1. Numbering Scheme in the 1,3-Bis(diethyl amide)-Substituted Calix[4]arene Ligand



pH <2 no extraction took place suggesting deprotonation of the 2- and 4-hydroxyl groups of the calix[4]arene ligand is crucial to the success of the extraction process. Presumably the dichloromethane organic phase contains solution lanthanide−**L** complex species (Ln(**L**-2H) picrate) with structures similar to the those of solid state complexes discussed earlier, in which the trivalent lanthanide cation is fully encapsulated in a polar environment within the lipophilic exterior of the calix[4]arene ligand. Solvent extraction of lanthanum using in the absence of picrate was carried out for comparison. However no extraction was discernable indicating that neither the nitrate or carbonate anion were participating in the extraction process, thus establishing the crucial role of the picrate anion in the extraction process.

Chart 2. Numbering Scheme in the Picrate Anion



Conclusions

The synthesis and structure determinations of lanthanum, samarium, ytterbium, and lutetium complexes of a 1,3-bis(diethyl amide) lower rim substituted calix[4]arene ligand **L** have been achieved. The structures exhibit similar features with the lanthanide cation being fully encapsulated in an eight-coordinate polar environment, consisting of six oxygen donor atoms from the calix lower rim and in the case of lanthanum a water molecule and a unidentate O^--picrate, and for samarium, ytterbium and lutetium a picrate anion chelating in a bidentate arrangement. Solvent extraction studies revealed that under optimised conditions the calix[4]arene ligand **L** displayed generally very high percentage extractabilities of lanthanide cations which may be attributed to the calixarene's unique lower rim lanthanide coordination sphere environment and lipophilic exterior.

Acknowledgment. This work was supported by A.W.E. (plc.). Funds for the Image Plate system were obtained from

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(23) Under identical experimental extraction conditions to those used with L, dicyclohexano-18-crown-6 gave very poor extraction of lanthanides, <5%.

(24) Inoue, Y.; Nakagawa, K.; Hakushi, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2279.

(25) [Er(**L**-2H)(picrate)], CH_2Cl_2· EtOH·$2H_2O$, triclinic, space group $P\bar{1}$, $a = 14.093(8)$ Å, $b = 15.087(9)$ Å, $c = 18.228(9)$ Å, $\alpha = 87.72(1)°$, $\beta = 80.82\ (1)°$, $\gamma = 72.48(1)°$, $U = 3648.4$ Å^3. [Tm(**L**-2H)(picrate)]·$2.5CH_2Cl_2$·H_2O, triclinic, space group $P\bar{1}$, $a = 14.100(8)$ Å, $b = 15.136(9)$ Å, $c = 18.201(9)$ Å, $\alpha = 88.08(1)°$, $\beta = 81.11(1)°$, $\gamma = 72.10\ (1)°$, $U = 3651.5$ Å^3. [Pr(**L**-H)(picrate)]·EtOH, monoclinic, space group $C2/c$, $a = 29.853(8)$ Å, $b = 12.677(9)$ Å, $c = 40.641(18)$ Å, $\beta = 110.36(1)°$, $U = 14419.73$ Å^3.

(26) Various sources list different values for the radii of the lanthanides. We have therefore carried out a survey of lanthanide metal complexes in the Cambridge Crystallographic DataCentre and have calculated the average M−O bond lengths excluding complexes with unusually high or low coordination numbers. To ensure that the mean values were not biased by outliers, M−O bond lengths that differed from the mean by more than 4σ were excluded. Mean values (Å) were as follows: La, 2.66; Ce, 2.63; Pr, 2.59; Nd, 2.62; Sm, 2.50; Eu, 2.55; Gd, 2.49; Tb, 2.53; Ho, 2.48; Er, 2.47; Tm, 2.43; Yb, 2.33; Lu, 2.41.

(27) There are 23 examples in the Cambridge Crystallographic Database of the picrate anion bonded in a bidentate fashion to a lanthanide metal. All show the bond to the phenoxide oxide significantly shorter than the bond to the nitro oxygen (mean values 2.344, 2.694 Å, respectively).

(28) Search of the Cambridge Crystallographic Database show coordination numbers ranging from 3 to 12. Disregarding structures involving organometallic La−C bonds we find that coordination numbers 8 and 9 are the most frequently observed each with over 30% of the total. We calculate the mean coordination number as 8.12.

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Supporting Information Available: Text detailing the structure solution and tables of crystal data, atomic coordinates, and molecular dimensions, anisotropic thermal parameters, for the four structures. Details for [La(**L**-2H)(picrate)H_2O)]3MeCN,CH_2Cl_2 (**1**) are given in Tables S1−S5, for [Sm(**L**-2H)(picrate)]EtOH (**2**) in Tables S6−S10, for [Yb(**L**-2H)(picrate)]3CH_2Cl_2,H_2O, (**3**) in Tables S11−S15 and for [Lu(**L**-2H)(picrate)] CH_2Cl_2,EtOH,H2O (**4**) in Tables S16-S20 (52 pages). Ordering information is given on any current masthead page.

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