Neutral lanthanide di- and mono-meric complexes and selective extraction properties of a new 1,3-acid-diethyl amide substituted calix[4]arene ligand

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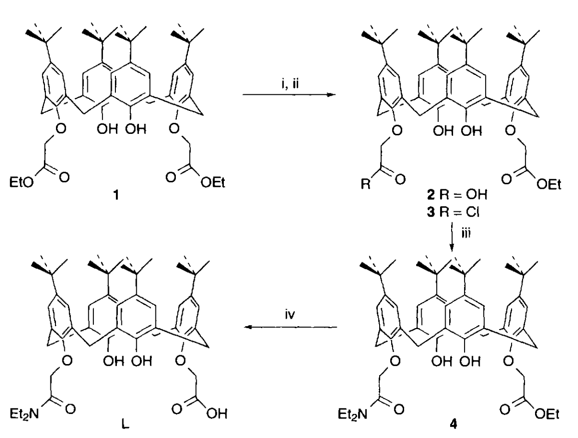
The synthesis, X-ray crystal structures of neutral dimeric europium, samarium and monomeric lutetium complexes, and selective extraction properties of a new 1,3-acid-diethyl amide substituted calix[4]arene ligand L are described.

The calixarenes[1] are a class of synthetic macrocyclic receptors that can be modified at the phenolic lower rim with additional oxygen donor atoms to produce various ionophores[2] capable of binding alkali-, and alkaline-earth-metal and lanthanide cations.[3–6] Many of these calixarene derivatives contain ionisable phenol or carboxylate groups that at relatively high pH values favour binding of the lanthanide cations, over alkali- and alkaline-earth-metal cations.[4] Surprisingly the majority of lanthanide–calixarene complexes reported are charged entities requiring counter anions for neutrality.[7] In light of this we have initiated a research programme aimed at preparing new efficient and selective extraction reagents for lanthanides and describe here the synthesis, single-crystal structures of neutral dimeric europium, samarium and monomeric lutetium complexes and selective extraction properties of a new 1,3-acid-diethyl amide substituted calix[4]arene ligand L.

The 1,3-bis(ethylcarboxy)calix[4]arene derivative (**1**)[8] was selectively monohydrolysed by addition of 1 equiv. of KOH in refluxing ethanol. Upon reaction with $SOCl_2$ the ester-acid compound (**2**) was converted to the ester-acid chloride derivative (**3**) which on addition of excess $NHEt_2$ gave the amide-ester (**4**) in 72% overall yield. (Scheme 1). Selective hydrolysis of the ester group using KOH in ethanol gave L as a white powder (Scheme 1).

The addition of $Ln(NO_3)_3{\cdot}nMe_2SO$ (n = 3, 4) (Ln = Eu, Sm, Lu) to L in dmf and excess NEt_3 precipitated the respective lanthanide complexes. Crystals suitable for X-ray crystallographic determination were isolated from dilute dichloromethane–ethanol (Eu, Sm) and dmf (Lu) solutions of the respective complexes.†



Scheme 1 *Reagents and conditions*: i, 1 equiv. KOH, EtOH; ii, $SOCl_2$, CH_2Cl_2; iii, $NHEt_2$, NEt_3, CH_2Cl_2; iv, KOH in EtOH

The structures of the lutetium monomer and the europium dimer are shown in Figs. 1 and 2 respectively together with the

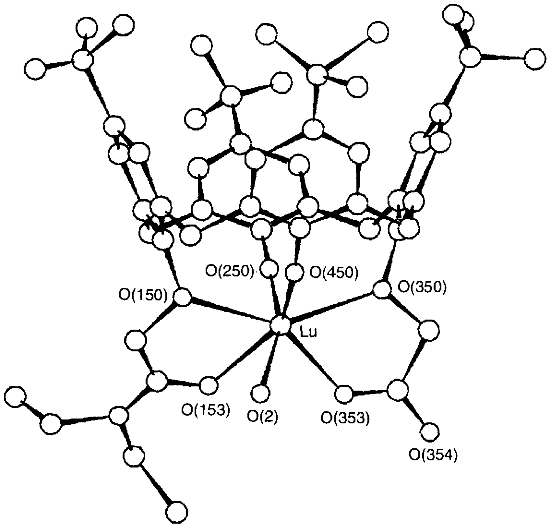


Fig. 1 The structure of the $[LuL(H_2O)]$ monomer. Bond lengths (Å) in the metal coordination sphere: Lu–O(250) 2.066(8), Lu–O(450) 2.053(7), Lu–O(150) 2.322(7), Lu–O(350) 2.418(7), Lu–O(353) 2.215(7), Lu–O(153) 2.338(8), Lu–O(2) 2.280(8).

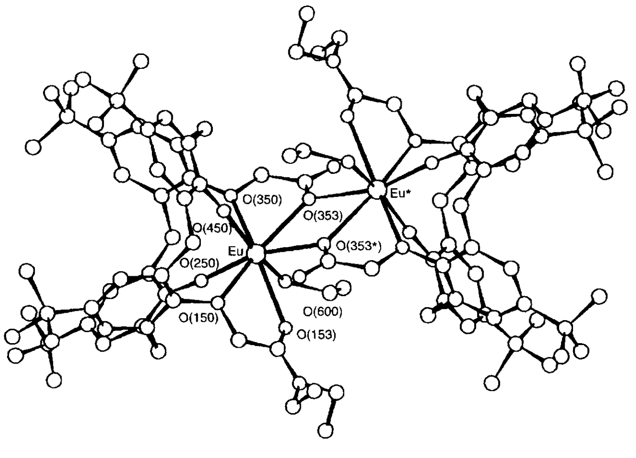


Fig. 2 The structure of the $[Eu_2L_2(HOEt)_2]$ dimer. Bond lengths (Å) in the metal coordination sphere: Eu–O(250) 2.169(14), Eu–O(450) 2.126(13), Eu–O(150) 2.57(2), Eu–O(350) 2.528(11), Eu–O(153) 2.51(2), Eu–O(353) 2.51(2), Eu–O(353*) 2.51(2), Eu–O(600) 2.55(2). Comparable distances in the Sm dimer are Sm–O(250) 2.155(8), Sm–O(450) 2.197(7), Sm–O(150) 2.569(7), Sm–O(350) 2.519(7), Sm–O(153) 2.470(7), Sm–O(353) 2.488(6), Sm–O(353*) 2.495(7), Sm–O(600) 2.524(10).

atomic numbering scheme. In both structures the substituted calix[4]arenes take up the common cone conformation. In the monomer the lutetium atom is bonded to the four oxygen atoms at the bottom of the cone O(150), O(250), O(350), O(450), to a carbonyl oxygen of the amide O(153) and to an oxygen of the acid O(353). The coordination sphere of seven donor atoms is completed by a water molecule O(2).

By contrast in the centrosymmetric dimer, the metal atoms are eight-coordinate, being bonded to the four oxygen atoms at the bottom of the cone, O(150), O(250), O(350), O(450), to a carbonyl oxygen of the amide O(153) and to two bridging oxygen atoms of the two acid linkages O(353), O(353*). The coordination sphere is completed by an ethanol molecule O(600). The structure of the samarium dimer is equivalent to that of the europium dimer.

It is clear that the difference in structure is due to the size of the metal cation with the larger Eu, Sm lanthanides forming the eight-coordinate dimeric structure, and the smaller Lu lanthanide forming the seven-coordinate monomer structure. These solid-state crystallographic results are in agreement with molecular-modelling studies which suggest the larger lanthanides (La–Eu) preferentially form dimeric isomorphic structures and the smaller lanthanides (Gd–Lu) discrete monomeric complexes with L.[‡]

Lanthanide extraction experiments were carried out using optimised conditions of the aqueous phase containing lanthanide nitrate (0.4×10^{-3} mol dm^{-3}) at pH = 5.8 with citrate buffer,[§] and the extractant dichloromethane solvent phase containing L at a concentration of 9.6×10^{-3} mol dm^{-3}. Equal volumes (10 ml) of each solution were mixed and rapidly stirred for 1 h and inductively coupled plasma atomic emission spectrometer (ICP-AES) analysis used to determine the concentrations of lanthanide in the respective phases. The extraction results with La^{3+}, Eu^{3+}, Tm^{3+} and Lu^{3+} (Fig. 3) clearly show a selectivity preference for the larger lanthanides in the order of decreasing extraction efficiency $La^{3+} > Eu^{3+} > Tm^{3+} > Lu^{3+}$. It is noteworthy that the extraction data are consistent with the fact that the formation of the dimer complex with L, may be crucial to the efficient extraction of the lanthanide metal.

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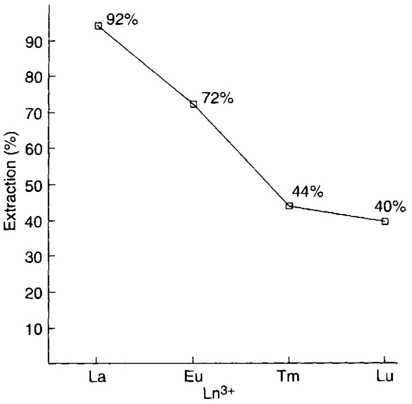

Fig. 3 Graphical representation of extraction data for L and lanthanides; Ln : L : citrate = 1 : 24 : 3, pH = 5.8

Footnotes

[†] *Crystal data*: for $[Lu(L - 3H)(OH_2)]\cdot Me_2SO\cdot 0.5EtOH\cdot 1.5H_2O$, $C_{55}H_{80}LuNO_{11}S$, $M = 1138.2$, monoclinic, space group $C2/c$, $a = 32.79(2)$, $b = 17.054(12)$, $c = 28.66(2)$ Å, $\beta = 124.17(1)°$, $U = 13259(16)$ Å^3, $Z = 8$, $D_c = 1.140$ Mg m^{-3}, $\mu = 1.570$ mm^{-1}, $F(000) = 4736$, independent reflections collected 7919, ($R_{int} = 0.045$), refinement method full-matrix least-squares on F^2. Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0527$, $wR2 = 0.1745$.

For $[Eu_2(L - 3H)_2(HOEt)_2]\cdot 2CH_2Cl_2\cdot C_2H_5OH$, $C_{112}H_{156}Cl_4Eu_2N_2O_{17}$, M 2248.1, triclinic, space group $P\bar{1}$, $a = 13.136(7)$, $b = 12.839(8)$, $c = 20.869(11)$ Å, $\alpha = 96.62(1)$, $\beta = 96.29(1)$, $\gamma = 119.11(1)°$, $U = 2998.2$ Å^3, $Z = 1$, $D_c = 1.245$ Mg m^{-3}, $\mu = 1.184$ mm^{-1}, $F(000) = 1172$, 9365 independent reflections calculated, final R 0.1026, $wR2 = 0.3121$.

For $[Sm_2(L - 3H)_2(HOEt)_2]\cdot 4CH_2Cl_2\cdot 2C_2H_5OH$, $C_{116}H_{164}Cl_8N_2O_{18}Sm_2$, M 2458.8, triclinic, space group $P\bar{1}$, $a = 13.070(8)$, $b = 13.468(8)$, $c = 21.416(11)$ Å, $\alpha = 99.11(1)$, $\beta = 101.29(1)$, $\gamma = 119.14(1)°$, $U = 3084.1$ Å^3, $Z = 1$, $D_c = 1.324$ Mg m^{-3}, $\mu = 1.184$ mm^{-1}, $F(000) = 1278$, 8714 independent reflections calculated, final R 0.0764, $wR2 = 0.2284$.

Data for the three structures were measured on a Marresearch Image Plate system. The crystals were positioned at 75 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[9] Heavy-atom positions were obtained from Patterson functions and Fourier methods were used to locate all remaining atoms. All structures contained solvent, some of which was disordered. The structures were refined, (non-hydrogen atoms in the complex, anisotropic, solvent atoms and hydrogen atoms isotropic) by full-matrix least squares on F^2 using SHELXL.[10]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/55.

[‡] Elemental analytical data for isolated La, Pr and Tm lanthanide complexes of L substantiate the modelling predictions.

[§] Analogous extraction experiments in the absence of citrate gave similar extraction percentage efficiencies suggesting citrate is not taking an active role in the extraction process.

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