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First- and second-sphere co-ordination of a lanthanum cation by a calix[4]arene tetraamide in the partial-cone conformation

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5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(diethylcarbamoylmethoxy)calix[4]arene (L) has been synthesized in the partial-cone conformation for the first time. Reaction with lanthanum picrate (2,4,6-trinitrophenolate) gives a 1:1 complex which has been structurally characterised: $[LaL(pic)_3(H_2O)_2]\cdot 3H_2O\cdot MeCN$ (triclinic, space group $P\bar{1}$, $Z = 2$, $R = 0.087$ for 10 150 independent reflections above background). The metal–calixarene interactions involve two amide oxygen atoms in the first co-ordination sphere and three oxygen atoms (two ether and one amide) in the second. The remainder of the first co-ordination sphere of the nine-co-ordinate lanthanum cation consists of two water oxygen atoms and oxygen atoms of the three picrate anions.

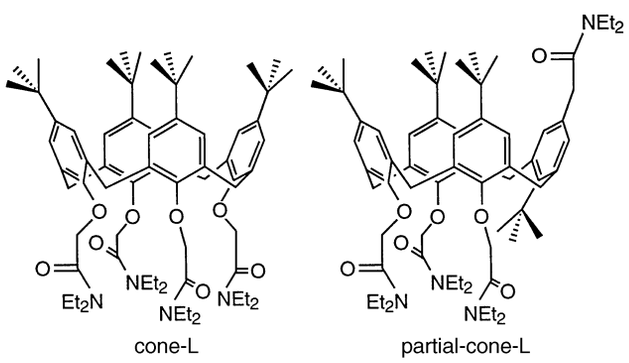
The macrocyclic framework of calix[4]arene has been functionalised in many ways to produce ionophores with widely varying properties.[1,2] One of the simplest and most widely studied means of functionalisation in alkylation of the phenol oxygen atoms.[3,4] Where the substituents at O are bulkier than the ethyl group such a reaction can give rise to four different conformers (cone, partial cone, 1,2-alternate and 1,3-alternate) which cannot readily interconvert.[5] Although all four conformations have been synthesized and isolated for some systems,[6] a general method applicable to any substituent has not been found to date.[3]

We are interested in amide-functionalised calix[4]arenes as receptors for metal cations and have previously described metal complexes of the calix[4]arene tetraamide (L) in the cone[7] and 1,3-alternate[8] conformations. We report here the synthesis of L in the partial-cone conformation and the synthesis and structural characterisation of a lanthanum picrate (2,4,6-trinitrophenolate, pic) complex, which exhibits simultaneous first- and second-sphere co-ordination of the lanthanum cation by the calixarene ligand.

Experimental

Syntheses

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(diethylcarbamoylmethoxy)calix[4]arene in the partial-cone conformation (partial-cone L) was prepared as follows. *p*-*tert*-Butylcalix[4]arene (3.0 g, 4.6 mmol) and Cs_2CO_3 (4.8 g, 25 mmol) were stirred in dry acetone (100 cm^3) for 2 h. 2-Chloro-*N*,*N*-diethylacetamide (5.7 g, 25 mmol) and CsI (6.5 g, 25 mmol) were added and the mixture was heated to reflux for 3 d. The solvent was removed under reduced pressure, and the remaining solid extracted into CH_2Cl_2 (2 × 100 cm^3). The CH_2Cl_2 solution was washed with 1 mol dm^{-3} HCl (100 cm^3) and water (2 × 100 cm^3). The solvent was then removed under reduced pressure, and the remaining solid dissolved in hot MeCN (100 cm^3). On cooling, a white solid precipitated (1.3 g, 25% yield) which was found to be L in the cone conformation. Subsequent crops of product from the mother-liquor gave the desired product (2.2 g, 43% yield) (Found: C, 73.5; H, 8.85; N, 6.15. Calc. for $C_{68}H_{100}N_4O_8\cdot CH_3CN$: C, 73.6; H, 9.1; N, 6.15%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.98, 1.07–1.14 (m each, 6 H, 18 H, CH_2CH_3), 1.01, 1.29, 1.33 [s each, 18 H, 9 H, 9 H, $C(CH_3)_3$], 3.11, 3.84, 3.98, 4.86 (d each, 2 H each, CH_2 bridge), 3.14–3.26, 3.35–3.39 (m each, 8 H each, CH_2CH_3), 4.43, 4.45, 4.58, 4.72 (s, d, d, s, 2 H each, OCH_2CO), 6.54, 7.02, 7.03, 7.42 (br s, br s, s, s, 2 H each, aryl H).



The metal complex $[LaL(pic)_3(H_2O)_2]$ was prepared as follows. A solution of partial-cone L (0.022 g, 0.02 mmol) in CH_2Cl_2 (1 cm^3) was treated with an excess of $La(pic)_3\cdot 12H_2O$[9] (0.052 g, 0.05 mmol) in MeCN (2 cm^3). Upon slow evaporation of the CH_2Cl_2, large yellow crystals precipitated in approximately 90% yield (Found: C, 52.5; H, 5.8; N, 9.35. Calc. for $C_{86}H_{110}LaN_{13}O_{31}$: C, 52.7; H, 5.65; N, 9.3%). Attempts to prepare the analogous complex of cone-L under the same conditions resulted in reprecipitation of free cone-L.

Crystallography

Crystal data. $[LaL(pic)_3(H_2O)_2]\cdot 3H_2O\cdot MeCN$, $C_{89}H_{119}LaN_{13}O_{34}$, $M = 2053.9$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 14.244(11)$, $b = 14.901(13)$, $c = 25.799(22)$ Å, $\alpha = 102.80(1)$, $\beta = 102.61(1)$, $\gamma = 97.47(1)°$, $U = 5117$ Å^3, $D_c = 1.333$ Mg m^{-3}, $\mu = 0.501$ mm^{-1}, $F(000) = 2146$, crystal size 0.35 × 0.20 × 0.20 mm.

14 428 Independent reflections were measured with Mo-Kα radiation (λ 0.710 73 Å) using the MARresearch image-plate system. The crystal was positioned 75 mm from the image plate. Ninetyfive frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[10] The structure was solved from the Patterson function using the SHELXS 86 program.[11] In the calix[4]arene one of the *tert*-butyl groups was considered to be disordered and two sets of methyl groups were refined with 50% occupancy. In the metal complex the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters

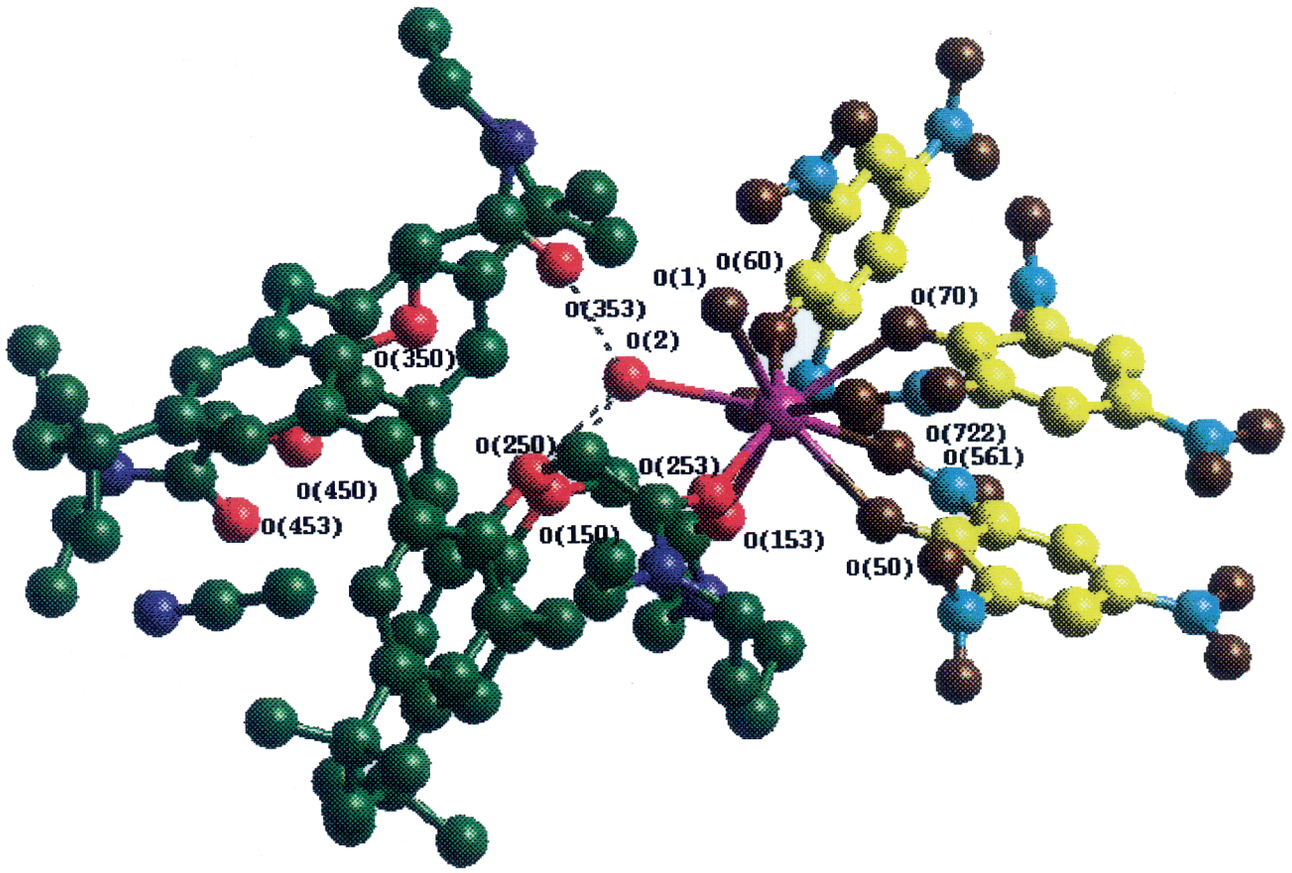


Fig. 1 Structure of $[LaL(pic)_3(H_2O)_2]\cdot 3H_2O\cdot MeCN$, together with part of the atomic numbering scheme. The lattice waters are not shown. Colours: lanthanum, purple; calixarene, carbon green, oxygen, red; picrates, carbon yellow, nitrogen light blue, oxygen brown; water bonded to lanthanum brown, water bonded to lanthanum and hydrogen bonded (shown as dashed lines) to the calixarene, red

equivalent to 1.2 times those of the atom to which they were attached. One solvent methyl cyanide molecule, four water molecules which were given 50% occupancy and one with full occupancy were all located. Solvent atoms were refined isotropically. No absorption correction was applied. The structure was then refined on F^2 using SHELXL[12] to an $R1$ of 0.0865 for 10 150 reflections with $I > 2\sigma(I)$. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/458.

Discussion

The reaction of *p-tert*-butylcalix[4]arene and 2-chloro-*N*,*N*-diethylacetamide in the presence of caesium carbonate has been found to produce the calix[4]arene tetraamide in both the cone and partial-cone conformations in an approximately 1:2 ratio. This contrasts with the analogous reaction with ethyl bromoacetate, where the use of caesium carbonate as base is reported to give 100% selectivity for the partial-cone conformer of the tetraester.[6] Fortunately, the cone and partial-cone conformations produced in the present reaction were readily separated by virtue of their differing solubilities in methyl cyanide. To our knowledge, this is the first example of a calix[4]arene tetraamide synthesized in the partial-cone conformation. The ^{1}H NMR spectrum of partial-cone-L is similar to that of the analogous tetraester derivative; the bridging methylene protons appear as two pairs of doublets, which is characteristic of the partial-cone conformation.[6]

The synthesis of the lanthanum picrate complex of the partial-cone-L was readily achieved by combining the ligand and metal salt in a dichloromethane–methyl cyanide solvent mixture. It is interesting that the same reaction with cone-L resulted in the precipitation of the free calixarene; this may be because the complete encapsulation of the metal cation so that it is bonded to all eight oxygen atoms of the calix[4]arene, as previously observed in structural studies of complexes of cone-L,[7,13,14] where the metal requires dissociation of all three picrate anions which may not be favoured in the solvents used here. Microanalytical results were consistent with the formation of a 1:1 complex, with the formulation $[LaL(pic)_3(H_2O)_2]$ and this was confirmed by the crystallographic study.

The structural analysis shows (Fig. 1, Table 1) that the lanthanum is nine-co-ordinate being bonded to only two atoms of the calix[4]arene, both carbonyl oxygen atoms [La–O(153) 2.439(7), La–O(253) 2.435(6) Å]. The metal is also bonded to two water molecules [O(1), 2.582(8); O(2), 2.613(6) Å] and five oxygen atoms from three picrate ions. For the picrates, all three phenolic oxygen atoms are bonded quite strongly to the metal [O(50), 2.466(8); O(60), 2.376(7); O(70), 2.447(7) Å]. Two of the picrates are also weakly bonded to the metal *via* a nitrate oxygen atom [O(561), 2.769(9); O(722), 2.854(9) Å]. The third picrate has a second contact from O(261) but this distance of 3.506 Å cannot be considered to be a bond. The picrate anions are significantly non-planar with the angles of nitrates with the phenyl rings being 75.6, 1.5, 33.2; 22.1, 9.4, 34.9; and 20.1, 6.7, 61.0° respectively.

A solvent methyl cyanide molecule is found in the cavity of the calixarene defined by three aromatic rings and one of the diethylamide moieties. The inclusion of this solvent is often found in the cone conformation of calix[4]arenes[7,15] but this is the first time to our knowledge that it has been structurally characterised in the partial-cone conformation. Other structur-

Table 1 Dimensions in the metal co-ordination sphere (distances in Å, angles in °)

La–O(60)	2.376(7)	La–O(1)	2.582(8)
La–O(253)	2.435(6)	La–O(2)	2.613(6)
La–O(153)	2.439(7)	La–O(561)	2.769(9)
La–O(70)	2.447(7)	La–O(722)	2.854(9)
La–O(50)	2.466(8)		
O(60)–La–O(253)	149.0(2)	O(70)–La–O(2)	145.7(2)
O(60)–La–O(153)	83.2(3)	O(50)—O(2)	133.8(2)
O(253)–La–O(153)	78.9(2)	O(1)–La–O(2)	68.3(2)
O(60)–La–O(70)	122.0(2)	O(60)–La–O(561)	137.0(3)
O(253)–La–O(70)	79.3(2)	O(253)–La–O(561)	69.1(2)
O(153)–La–O(70)	79.7(2)	O(153)–La–O(561)	137.8(2)
O(60)–La–O(50)	78.4(3)	O(70)—O(561)	68.1(3)
O(253)–La–O(50)	130.5(2)	O(50)—(561)	61.4(2)
O(153)–La–O(50)	139.9(2)	O(1)—O(561)	61.4(2)
O(70)–La–O(50)	80.5(2)	O(2)—O(561)	124.4(2)
O(60)–La–O(1)	101.0(3)	O(60)–La–O(722)	62.4(2)
O(253)–La–O(1)	75.9(2)	O(253)–La–O(722)	131.8(2)
O(153)–La–O(1)	136.0(2)	O(153)–La–O(722)	70.5(3)
O(70)–La–O(1)	128.8(3)	O(70)–La–O(722)	59.7(2)
O(50)–La–O(1)	82.8(3)	O(50)–La–O(722)	69.5(3)
O(60)–La–O(2)	73.1(2)	O(1)–La–O(722)	149.7(3)
O(253)–La–O(2)	77.3(2)	O(2)–La–O(722)	123.5(2)
O(153)–La–O(2)	71.4(2)	O(561)–La–O(722)	112.0(2)

ally characterised calix[4]arenes in the partial-cone conformation containing solvent molecules in this cavity appear to be rare,[16,17] although the silver cation complexes of tetra-*O*-alkylcalix[4]arenes in the partial-cone conformation have been characterised where the metal cation resides in the hydrophobic cavity (the metal cation can be displaced in some cases by solvents such as methyl cyanide).[18,19] 'Self-inclusion' of the phenol substituent of the inverted aromatic ring has also been noted.[17] The conformation of the partial cone is as expected with the four phenyl rings making angles of 63.0, 62.8, 70.8 and 78.3° with the plane of the four methylenes.

Of importance in stabilising the complex are intramolecular hydrogen bonds. Specifically, O(2) which is bonded to the metal also forms three strong hydrogen bonds to the calixarene, two ethereal oxygen atoms O(150) at 2.742 and O(250) at 2.826 Å that are part of the amide groups that are bonded to the metal and O(353) at 2.709 Å, so that the calixarene is bound to the first *and* second co-ordination spheres[20] of the lanthanum cation. Thus these two amide groups form a compact unit around the metal. A water molecule not bonded to the metal, O(3), is also in the second co-ordination sphere of the lanthanum cation being hydrogen bonded to O(1) at 2.695, O(453) at 2.658 (symmetry operation $x + 1$, y, z) and O(561) at 2.695 Å.

While further structural studies will be required to elucidate the influence of cation size and ligand structure on the nature of the complex formed, the results described here suggest calixarenes may be a useful framework for constructing ligands capable of simultaneous first- and second-sphere co-ordination of lanthanide cations, a structural feature which has been largely confined to transition-metal complexes to date,[20] although a somewhat analogous example has been reported for $Na[Eu_3L'_2(H_2O)_{18}(ONC_5H_5)_3]\cdot 14H_2O$ (L′ = *p*-sulfonatocalix[4]arene).[21]

Acknowledgements

We thank the EPSRC and the University of Reading for funds for the image plate system and A.W.E. plc for funding of this work. We thank Antony Richards (M.S.I.) for his help in preparing Fig. 1.

References

1 M. A. McKervey, M.-J. Schwing-Weill and F. Arnaud-Neu, in *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. Macnicol and F. Vögtle, Pergamon, New York, 1996, vol. 1, ch. 15, p. 537.
2 C. D. Gutsche, *Calixarenes*, ed. J. F. Stoddart, Royal Society of Chemistry, Cambridge, 1989.
3 V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713.
4 D. M. Roundhill, *Prog. Inorg. Chem.*, 1995, **43**, 533.
5 K. Iwamoto, K. Araki and S. Shinkai, *J. Org. Chem.*, 1991, **56**, 4955.
6 K. Iwamoto and S. Shinkai, *J. Org. Chem.*, 1992, **57**, 7066.
7 P. D. Beer, M. G. B. Drew, P. B. Leeson and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1995, 1273.
8 P. D. Beer, M. G. B. Drew, P. A. Gale, P. B. Leeson and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1994, 3479.
9 J. M. Harrowfield, W. M. Lu, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1994, **47**, 321.
10 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
11 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
12 G. M. Sheldrick, SHELXL, package for crystal structure refinement, University of Göttingen, 1993.
13 A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, G. D. Andreetti, G. Calestani and F. Ugozzoli, *J. Inclusion Phenom.*, 1988, **6**, 119.
14 N. Muzet, G. Wipff, A. Casnati, L. Domiano, R. Ungaro and F. Ugozzoli, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1065.
15 M. A. McKervey, E. M. Seward, G. Ferguson and B. L. Ruh, *J. Org. Chem.*, 1986, **51**, 3581.
16 P. D. J. Grootenhuis, P. A. Kollman, L. C. Groenen, D. N. Reinhoudt, G. J. van Hummel, R. Ugozzoli and G. D. Andreetti, *J. Am. Chem. Soc.*, 1990, **112**, 4165.
17 S. Pappalardo, *New J. Chem.*, 1996, **20**, 465.
18 A. Ikeda, H. Tsuzuki and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2073.
19 W. Xu, R. J. Puddephatt, K. W. Muir and A. A. Torabi, *Organometallics*, 1994, **13**, 3054.
20 S. J. Loeb, in *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. Macnicol and F. Vögtle, Pergamon, New York, 1996, vol. 1, ch. 20, p. 733.
21 J. L. Atwood, G. W. Orr and K. D. Robinson, *Supramol. Chem.*, 1994, **3**, 89.

Received 27*th November* 1996; *Paper* 6/08029D