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ORIGINAL ARTICLE

The extraction of thallium(I) and silver(I) ions with 1,3-alternate calix[4]arene derivatives

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Abstract Tetraallyloxy and tetrabenzyloxy derivatives of calix[4]arenes in cone and 1,3-alternate conformations were synthesised and their capacity to extract thallium(I) and silver(I) ions was investigated. 'Low'-temperature single crystal X-ray structure determinations were recorded for two derivatives in which the calixarene conformation was that of an alternating cone, the aromatic rings lying closely quasi-parallel to the $\overline{4}$-axis of the cone. The structure of a tetraallyloxy derivative in the cone conformation was also determined in which a molecule of acetonitrile was included within the calixarene cavity.

Keywords Calix[4]arene · Thallium(I) · Soft metals · 1,3-Alternate · Solvent extraction

Introduction

The calixarenes are well-known macrocyclic compounds that have been studied extensively for host–guest chemistry [1, 2]. They can be readily functionalised through the phenolic groups or directly on the aromatic ring and this has resulted in the design and synthesis of a variety of derivatives for a wide range of functions [3–6]. One of the more widely studied areas of calixarene chemistry is their use as ionophores for both cations and anions [7–9]. This has resulted in applications in ion selective electrodes [10, 11], metal extraction [12–14] and catalysis [5, 15]. The complexation and extraction of thallium(I) and silver(I) ions has been achieved using crown ethers [16, 17] and with calixarenes [18–20]. Beer has reported a calix-tube in which the thallium(I) ion is coordinated to the aromatic rings through π-metal complexation [21, 22].

Calixarenes have four main conformations: cone, partial cone, 1,2-alternate and 1,3-alternate. These different conformations can have a significant effect on the metal complexation properties of the ligand [23–26]. In this study we have compared the impact on the extraction of silver and thallium ions of the 1,3-alternate and cone conformations of a number of calixarene derivatives. We also report the impact of the presence of the *tert*-butyl group on the calixarene framework.

Experimental

Melting points were measured on an Electrothermal 9100 apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 NMR spectrometer (^{1}H 200 MHz and ^{13}C 50 MHz) with $CDCl_3$ as the solvent unless otherwise specified. The chemical shifts for ^{1}H NMR spectra are referenced to the peak due to the residual proton(s) in the solvent (δ 7.27 for $CDCl_3$, δ 3.31 for CD_3OD and δ 2.05 for $(CD_3)_2CO$), while those for the ^{13}C NMR spectra are referenced against the carbon signal in $CDCl_3$ (δ 77.0). Elemental analyses were performed by the Central Science Laboratory, University of Tasmania, Australia. Flame

Dedicated to Len Lindoy on the occasion of his 75th birthday and in recognition of his great contribution to the field of macrocyclic chemistry.

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atomic absorption spectroscopy (FAAS) was carried out on the Varian Spectra AA-10 Flame Atomic Absorption Spectrometer using the parameters suggested in the Varian Analytical Methods handbook.

Synthesis

$1^2,3^2,5^2,7^2$-Tetraallyloxy-$1^5,3^5,5^5,7^5$-tetra-*tert*-butylcalix[4]arene (**1**)[1] [27], $1^2,3^2,5^2,7^2$-tetrabenzyloxy-$1^5,3^5,5^5,7^5$-tetra-*tert*-butylcalix[4]arene (**2**) [27], and $1^2,3^2,5^2,7^2$-tetrabenzyloxycalix[4]arene (**3**) [28], were prepared according to literature methods.

*1,3-Alternate $1^2,3^2,5^2,7^2$-tetraallyloxy-$1^5,3^5,5^5,7^5$-tetra-tert-butylcalix[4]arene (**4**)*

Cesium carbonate (4.88 g, 15 mmol) was added to a solution of $3^2,7^2$-diallyloxy-$1^5,3^5,5^5,7^5$-tetra-*tert*-butylcalix[4]arene-$1^2,5^2$-diol (**8**) [18] (2.08 g, 3 mmol) in acetone (anhydrous, 120 mL) and stirred under nitrogen for 5 h. Allyl bromide (2.23 g, 18 mmol) was then added and the solution heated at reflux under nitrogen for 72 h. The reaction mixture was then filtered and the solid washed with dichloromethane (2 × 15 mL). The solvent was removed under reduced pressure and the resulting oil was crystallised by the addition of methanol (15 mL). The precipitate was recrystallised from chloroform/ethanol (1:5, 30 mL), and further purified by column chromatography (500:80:1 light petroleum 40–70 °C, toluene, ethyl acetate) to give the product as thin clear crystals (1.23 g, 1.5 mmol, 53%, m.p. 248 °C). Found C, 82.6% H, 9.3%; $C_{56}H_{72}O_4 \cdot \frac{1}{2}H_2O$ requires C, 82.2% H, 9.0%. ^{1}H NMR δ 1.24 (s, 36H, C(C**H**$_3$)$_3$) 3.72 (s, 8H, Ar–C**H**$_2$–Ar) 3.91 (d. 8H, J = 5.1 Hz, OC**H**$_2$) 4.90–4.92, 4.97–4.98 (2 m, 8H, C = C**H**$_2$) 5.56–5.73 (m, 4H, C**H**=) 6.95 (s, 8H, Ar–**H**). ^{13}C NMR δ 32.3 (C(**C**H$_3$)$_3$) 34.6 (C(**C**H$_3$)$_3$) 39.5 (Ar–**C**H$_2$–Ar) 72.1 (O**C**H$_2$) 116.0, 127.6, 134.1, 135.9, 144.5, 154.1 (Ar, C=C).

*1,3-Alternate $1^2,3^2,5^2,7^2$-tetrabenzyloxy-$1^5,3^5,5^5,7^5$-tetra-tert-butylcalix[4]arene (**5**)*

Cesium carbonate (4.88 g, 15 mmol) was added to a solution of $3^2,7^2$-dibenzyloxy-$1^5,3^5,5^5,7^5$-tetra-*tert*-butylcalix[4]arene-$1^2,5^2$-diol (**9**) [29] (0.53 g, 1 mmol) in acetone (anhydrous, 120 mL) and stirred under nitrogen for 5 h. Benzyl bromide (1.55 g, 9 mmol) was then added and the solution heated at reflux under nitrogen for 72 h. Workup as described above gave a cream solid which was further purified by column chromatography (5:1 light petroleum 40–70 °C, dichloromethane) to give the product as clear crystals (0.43 g, 0.43 mmol, 43%), m.p. 223.1–223.3 °C (lit 224–226 °C [28]). ^{1}H NMR δ 0.95 (s, 36H, C(C**H**$_3$)$_3$) 3.45 (s, 8H, Ar–C**H**$_2$–Ar) 4.54 (s, 8H, J = 5.1 Hz, OC**H**$_2$) 6.76 (s, 8H, Ar–**H**) 7.01-7.04 (m, 8H, Ar–**H**) 7.23–7.26 (m, 12H, Ar–**H**).

*1,3-Alternate $1^2,3^2,5^2,7^2$-tetraallyloxycalix[4]arene (**6**)*

Cesium carbonate (4.88 g, 15 mmol) was added to a solution of calix[4]arene-$1^2,3^2,5^2,7^2$-tetrol (**10**) [30] (0.96 g, 2 mmol) in acetone (anhydrous, 120 mL) and stirred under nitrogen for 5 h. Allyl bromide (1.46 g, 12 mmol) was then added and the solution heated at reflux under nitrogen for 72 h. Workup as above, followed by column chromatography (350:250:1:1 light petroleum 40–70 °C, chloroform, glacial acetic acid, ethyl acetate) gave the product as flat clear crystals (0.47 g, 1.0 mmol, 36%, m.p. 184–186 °C) Found C, 82.0% H, 6.8%; $C_{40}H_{40}O_4$ requires C, 82.2% H, 6.8%. ^{1}H NMR δ 3.59 (s, 8H, Ar–C**H**$_2$–Ar) 4.13–4.18 (m, 8H, OC**H**$_2$) 5.10–5.13, 5.15–5.17, 5.19–5.21 (3 m, 8H, C=C**H**$_2$) 5.82–6.01 (m, 4H, C**H**=) 6.65 (t, 4H, J = 7.3 Hz Ar–**H**) 6.98 (d, 8H, Ar–**H**). ^{13}C NMR δ 37.6 (Ar–**C**H$_2$–Ar) 72.3 (O**C**H$_2$) 116.6, 122.4, 131.7, 134.4, 134.7, 156.4 (Ar, C=C).

*1,3-Alternate $1^2,3^2,5^2,7^2$-tetrabenzyloxycalix[4]arene (**7**)*

Cesium carbonate (4.88 g, 15 mmol) was added to a solution of calix[4]arene-$1^2,3^2,5^2,7^2$-tetrol (**10**) [30] (0.98 g, 2 mmol) in acetone (anhydrous, 120 mL) and stirred under nitrogen for 5 h. Benzyl bromide (1.87 g, 11 mmol) was then added and the solution heated at reflux under nitrogen for 72 h. Workup as above, followed by column chromatography (100:100:3 light petroleum 40–70 °C, toluene, ethyl acetate) gave the product as clear crystals (1.07 g, 1.4 mmol, 59%, m.p. 199.1–199.9 °C (lit 191–193 °C [31])). ^{1}H NMR δ 3.59 (s, 8H, Ar–C**H**$_2$–Ar) 4.88 (s, 8H, OC**H**$_2$) 6.48 (m, 4H, Ar–H) 6.70 (d, 8H, J = 7.3 Hz Ar–**H**) 7.18–7.25 (m, 8H, benzyl Ar–**H**) 7.39–7.46 (m, 8H, benzyl Ar–**H**). ^{13}C NMR δ 37.9 (Ar–**C**H$_2$–Ar) 72.35 (O**C**H$_2$) 122.8, 127.5, 127.7, 128.5, 131.9, 134.5, 138.8, 156.5 (Ar).

Structure determinations

Diffraction data were measured on Bruker AXS (**6** and **7**) or Enraf–Nonius CAD4 (**1**) instruments using monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å, at T 150 K (296 K for **1**). Following multi-scan absorption corrections (for **6** and **7** only), and solution by direct methods, the structures were refined by full-matrix least squares on F^2, refining anisotropic displacement parameters for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Neutral atom complex scattering factors were employed

[1] Calixarene nomenclature follows that recommended by IUPAC. See: Favre et al. [36].

within the SHELXL 97 program [32]. Results are presented below and in Tables and the Figures, the latter showing non-hydrogen atoms with 50% (20% for **1**) probability amplitude displacement ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å. Full cif depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre, CCDC 819764–819766**.**

Crystal/refinement data

*1,3-Alternate $1^2,3^2,5^2,7^2$-tetraallyloxycalix[4]arene (**6**)* $C_{40}H_{40}O_4$, $M_r = 584.7$. Monoclinic, space group $P2_1/c$ (C_{2h}^5, *No.* 14), $a = 10.0969(7), b = 39.023(3), c = 16.6769(11)$ Å, $\beta = 91.155(1)^\circ$, $V = 6569.6(8)$ Å^3. D_c ($Z = 8$) = 1.182 g cm^{-3}. $\mu_{Mo} = 0.075$ mm^{-1}; specimen: 0.42 × 0.18 × 0.14 mm; $2\theta_{max} = 58^\circ$; reflections collected = 62855, independent reflections = 16513 ($R_{int} = 0.026$), reflections ($I > 2\sigma(I)$) = 12146; $R1 = 0.041$ ($I > 2\sigma(I)$), $wR2 = 0.109$ (all data), S = 1.05, $|\Delta\rho_{max}| = 0.24$ e Å^{-3}.

*1,3-Alternate $1^2,3^2,5^2,7^2$-tetrabenzyloxycalix[4]arene (**7**)* $C_{56}H_{48}O_4$, $M_r = 784.9$. Monoclinic, space group $P2_1/c$, $a = 15.088(3), b = 11.607(2), c = 24.560(4)$ Å, $\beta = 98.895(3)^\circ$, $V = 4249.4(13)$ Å^3. D_c ($Z = 4$) = 1.227 g cm^{-3}. $\mu_{Mo} = 0.076$ mm^{-1}; specimen: = 0.50 × 0.42 × 0.35 mm; $2\theta_{max} = 58^\circ$; reflections collected = 40991, independent reflections = 10611 ($R_{int} = 0.026$), reflections ($I > 2\sigma(I)$) = 7874; $R1 = 0.043$ ($I > 2\sigma(I)$), $wR2 = 0.126$ (all data), $S = 1.03$. $|\Delta\rho_{max}| = 0.27$ e Å^{-3}.

*$1^2,3^2,5^2,7^2$-Tetraallyloxy-$1^5,3^5,5^5,7^5$-tetra-tert-butylcalix[4]arene (**1**)* $C_{56}H_{72}O_4{\cdot}CH_3CN$, $M_r = 850.2$. Triclinic, space group $P\bar{1}$ (C_i^1, *No.* 2), $a = 11.313(6), b = 12.527(2), c = 19.968(3)$ Å, $\alpha = 95.12(2), \beta = 91.59(2), \gamma = 111.94(3)^\circ$, $V = 2609(2)$ Å^3. D_c ($Z = 2$) = 1.082 g·cm^{-3}. $\mu_{Mo} = 0.066$ mm^{-1}; specimen: 0.35 × 0.25 × 0.15 mm (capillary) (no correction); $2\theta_{max} = 50^\circ$; reflections collected = 11569, independent reflections = 9154 ($R_{int} = 0.039$), reflections ($I > 2\sigma(I)$) = 4348; $R1 = 0.085$ ($I > 2\sigma(I)$), $wR2 = 0.28$ (all data); $S = 1.07$. $|\Delta\rho_{max}| = 0.36$ e Å^{-3}. *t*-Butyl group 24 and allyl groups 21, 42 were modelled as disordered over pairs of sites with occupancies set at 0.5 after trial refinement.

Solvent extraction

The silver, sodium and thallium(I) picrates were prepared according to literature methods. [33, 34] The purity was determined by FAAS, and was found to be at least 98%.

Dichloromethane solutions of the calixarene ligands (5 mL, 3 mmol L^{-1}, saturated with H_2O) were shaken for 30 min with the picrate solution (5 mL, 3 mmol L^{-1}, H_2O saturated with dichloromethane), and left to equilibrate overnight. The aqueous phase was diluted to appropriate levels and analysed by FAAS at the most sensitive wavelength.

Results and discussion

It has been shown that thallium binds within the cavities of calixarenes through the aromatic π-electrons [21]. It was thought that the π-metal binding would be stronger if the distal aromatic rings in the calix[4]arene derivatives were parallel (or nearly so). In the 1,3-alternate conformation of calix[4]arenes the opposing aromatic rings are virtually parallel. Consequently we prepared the 1,3-alternate derivatives of tetra-allyloxy and tetrabenzyloxycalix[4]arenes to compare the impact of conformation on extractability of thallium and silver ions. Furthermore, Ikeda and Shinkai [20] have reported that the 1,3-alternate conformation of tetrapropoxycalix[4]arene derivatives has a higher metal extraction ability for silver ions than the analogous cone conformation.

The synthesis of the tetraalkoxy derivatives (**4** and **5**) in the 1,3-alternate conformations was achieved in a two-step process via the corresponding dialkoxy derivatives (**8** and **9**). We found this process allowed an easier purification of the desired 1,3-alternate derivatives. Direct alkylation of the parent *tert*-butylcalixarene (**11**) with cesium carbonate gave the desired product contaminated with a significant amount of the partial cone conformer. However, direct alkylation of the calixarene (**10**) using cesium carbonate gave the desired 1,3-alternate derivatives (**6** and **7**) in moderate yields.

The results of the 'low'-temperature single crystal X-ray studies are consistent, in terms of stoichiometry and connectivity, with the above formulations (Figs. 1, 2, 3); the *t*-butylated complex is an acetonitrile monosolvate. In each case (Figs. 1, 2, 3) the molecules lie within the crystal lattice with the axis of the calix[4]arene unit lying closely parallel to one of the actual or reciprocal crystallographic axes. Their relationships to each lattice overall, however, are quite different: for the parent calix[4]arene derivatives, in the case of the benzyl compound (**7**), one, in the case of the allyl derivative (**6**), two, molecule(s), devoid of crystallographic symmetry, comprise the asymmetric units of their structures. In the benzyl derivative, the molecules pack with similar rings in adjacent molecules lying parallel, being related by inversion centres or screw axes. Within the molecules the C–O–C–C–C torsions in three of the four pendant strings are *trans*, so that the plane of the phenyl ring of the pendant is *quasi*-normal to that of the parent aromatic ring of the calixarene; the dispositions of the allyl groups in that analogue are similar. In both of

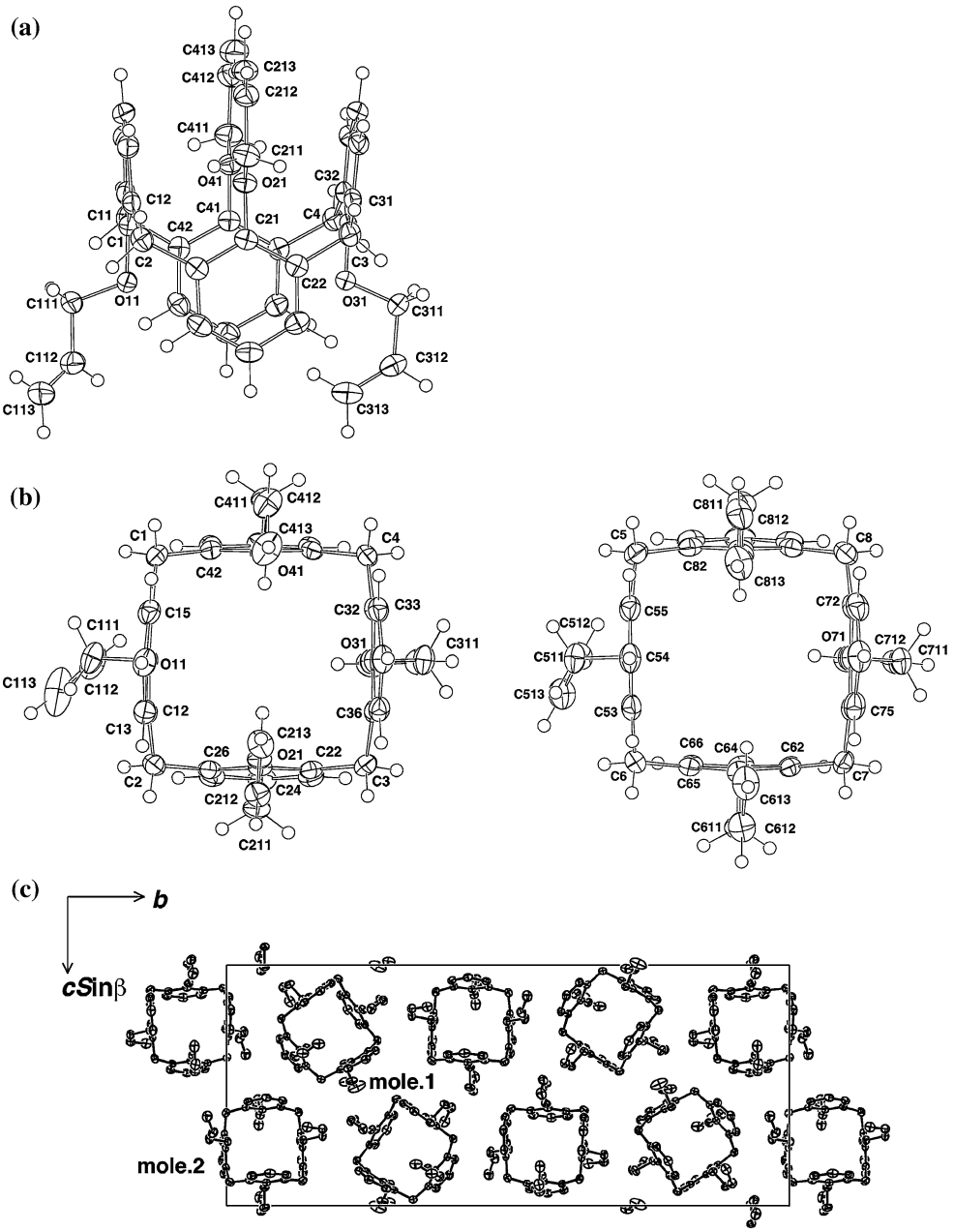


Fig. 1 **a** 'Side-on' projection of molecule 1 of 1,3-alternate $1^2,3^2,5^2,7^2$-tetraallyloxycalix[4]arene (6). **b** Projections of molecules 1, 2 down their central axes. **c** Unit cell contents, projected down *a*

those compounds, the directions of the aromatic rings and their substituents in all molecules are alternant. Despite their common orientation with their quasi-$\bar{4}$ - axes parallel to *a*, the molecules of the allyl complex pack in two independent sets, the set of molecule 2 lying with the aromatic rings of the calixarene unit quasi-parallel to *b* and *c**, while the set of molecule 1 are oblique to those axes (Fig. 1(c)). Nevertheless, within both molecules, the allyl conformations are similar (Fig. 1a), the terminal methylene groups of the pendants lying '*cis*' to the phenolic oxygen atoms and beneath them in projection down the molecular axes, while the fourth in each case lies skew-*trans*.

For the tetraallyloxycalix[4]arene derivative (**1**), a single formula unit comprises the asymmetric unit of the structure (Fig. 3). Disorder is found among the pendants of rings 2 and 4; the interplanar dihedral angle between the C_6 aromatic planes for those rings is 49.7(1)°, very similar to that between the planes of rings 1 and 3 which is 48.8(1)°; to the O_4 plane, the angles are 66.7(1), 64.1(1), 64.5(1) and 66.2(1)°. (In the parent $1^5,3^5,5^5,7^5$-tetra-*tert*-butylcalix[4]arene acetonitrile monosolvate, the latter angles are 58.0(2), 57.5(2), 58.4(2), 57.8(2)° [35]). Thus, despite the disorder, the array is an almost perfect cone. The cone is found to include the acetonitrile molecule of solvent,

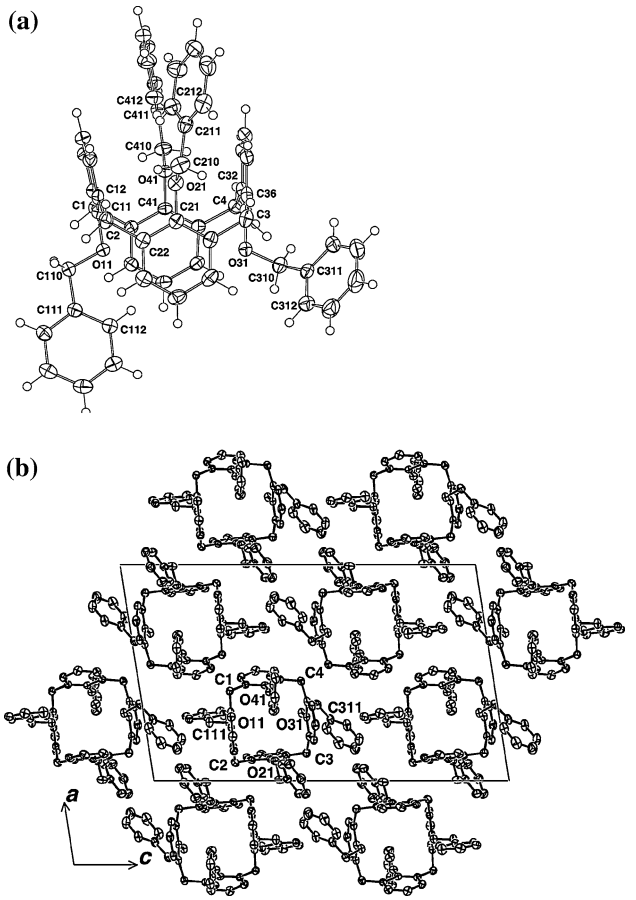


Fig. 2 **a** 'Side-on' projection of a molecule of 1,3-alternate $1^2,3^2,5^2,7^2$-tetrabenzyloxycalix[4]arene (**7**). **b** Unit cell contents, projected down *b*

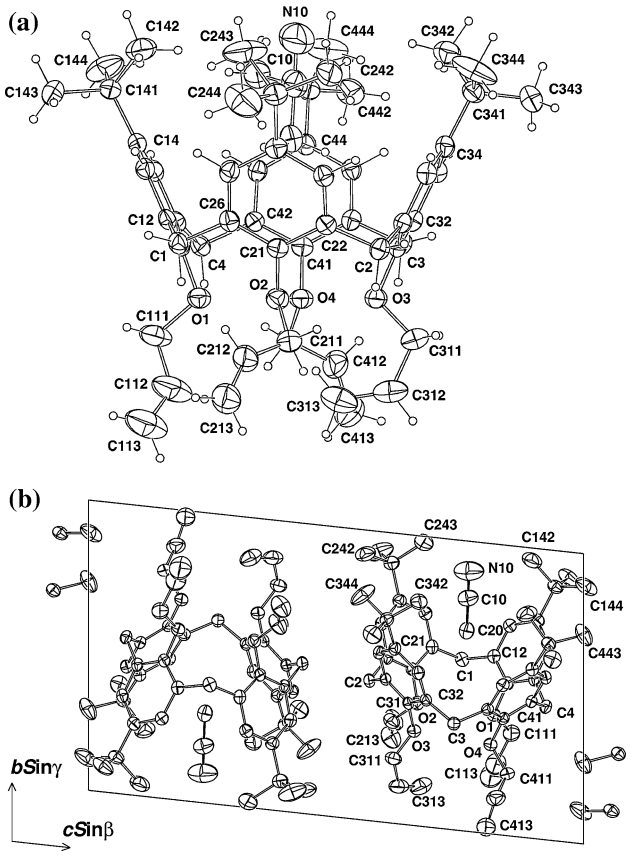
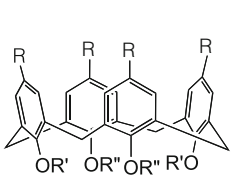
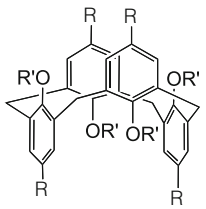


Fig. 3 **a** 'Side-on' projections of the molecule of $1^2,3^2,5^2,7^2$-tetraallyloxy-$1^5,3^5,5^5,7^5$-tetra-*tert*-butylcalix[4]arene (**1**).acetonitrile. **b** Unit cell contents, projected down *a*

aligned along the cone axis, the methyl end modelled as penetrating the core on the basis of refinement evidence.



(**1**) R = ^{t}Bu R' = R" = allyl
(**2**) R = ^{t}Bu R' = R" = benzyl
(**3**) R = H R' = R" = benzyl
(**8**) R = ^{t}Bu R' = H R" = allyl
(**9**) R = ^{t}Bu R' = H R" = benzyl
(**10**) R = H R' = R" = H
(**11**) R = ^{t}Bu R' = R" = H



(**4**) R = ^{t}Bu R' = allyl
(**5**) R = ^{t}Bu R' = benzyl
(**6**) R = H R' = allyl
(**7**) R = H R' = benzyl

A convenient method for evaluating the cation-binding ability of ligands is to determine their effectiveness in solvent extraction. Aqueous metal picrate solutions were extracted at room temperature (approximately 25 °C) with dichloromethane solutions of the calixarene derivatives (**2–7**). The percentage extractability is defined as the percentage of metal ion extracted from the aqueous phase, as determined by FAAS. The results are shown in Table 1. None of the calixarenes examined extracted sodium picrate and all showed low extractability for silver picrate, except for (**4**) which extracted 15% of the available silver picrate. The *tert*-butylcalixarene derivatives in the cone conformation (**1** and **2**) extracted slightly more thallium(I) than their 1,3-alternate analogues (**4** and **5**). In the cone

Table 1 Percentage extraction of metal picrates by calixarene derivatives

Compound	Sodium	Silver	Thallium
1[a]	0	6 ± 2	50 ± 2
2	0	2 ± 2	57.0 ± 0.5
3	0	4 ± 2	10 ± 1
4	0	15 ± 1	43 ± 2
5	0	3 ± 2	53 ± 1
6	0	7 ± 2	54 ± 2
7	0	1 ± 2	41 ± 3

[a] Value reported by Couton et al. [18]

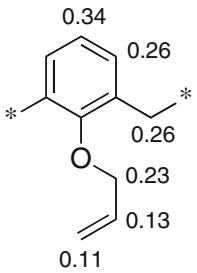


Fig. 4 Changes in the chemical shift ($\Delta\delta$) in the ^{1}H NMR spectrum of calixarene (6) on addition of 1.4 molar equivalent of thallium(I) triflate (only one monomer unit is shown for clarity)

conformation, the *tert*-butyl group was required for efficient extraction of thallium(I) as seen here with the tetrabenzyloxy derivatives (**2** and **3**) and reported previously for the tetraallyloxy analogues [18]. In contrast, in the 1,3-alternate derivatives, the presence or absence of the *tert*-butyl group had little impact on thallium(I) extractability.

The thallium binding characteristics for the 1,3-alternate calixarene (**6**) were investigated by ^{1}H NMR spectroscopy. As incremental amounts of thallium(I) triflate were added to a solution of the calixarene in deuterated acetone a gradual downfield peak movement was observed. This gradual downfield shift demonstrates the fast exchange kinetics on the NMR time scale. The changes in chemical shift ($\Delta\delta$) for the hydrogen atoms of calixarene (**6**) after the addition of 1.4 equivalents of thallium(I) triflate are summarised in Fig. 4.

The largest changes in chemical shift in the 1,3-alternate calixarene were associated with the aromatic hydrogen atoms, suggesting the metal is bound between the opposing aromatic rings with possible further coordination with the oxygen atoms of the allyl ethers of the adjacent rings. It is unlikely that the alkene of the allyl group is involved as the vinylic hydrogen atoms show the smallest chemical shift change in these experiments. One important difference between the 1,3-alternate calixarenes and the cone conformer is the potential to have two binding sites in the one molecule. Thus it was necessary to test the stoichiometry of the calixarene (**6**)/thallium triflate complex. This was achieved by an NMR continuous variations experiment, or Job's plot, with calixarene (**6**) and thallium(I) triflate which showed a maximum value 0.5 mol fraction of host. This indicated a 1:1 complex stoichiometry, demonstrating that only one side of the calixarene molecule is able to complex with thallium(I) at any one time. The two binding sites may be too close together to fit more than one thallium(I) ion as the repulsion of two positive ions becomes too great.

Conclusions

Tetraallyloxy and tetrabenzyloxy derivatives of calix[4]arenes in cone and 1,3-alternate conformations were synthesised and their capacity to extract thallium(I) and silver(I) ions was investigated. The low-temperature single crystal X-ray structures of three calixarene derivatives have been reported, two in the 1,3-alternate conformation and one in the cone conformation. The solvent extraction results for the *tert*-butylcalixarene derivatives showed, somewhat surprisingly, that the conformation had little impact on the extractability of thallium(I) ions. The tetraallyloxy derivatives in the cone conformation did show increased extractability for silver ions over their cone analogues. The conformation of the calixarene was important in the case of the "de-butylated" calixarenes. Here there was a significant increase in extractability for both silver and thallium(I) ions when using the 1,3-alternate conformation.

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