Cation complexation by chemically modified calixarenes. Part 10. Thioamide derivatives of *p-tert*-butylcalix[4]-, [5]- and [6]-arenes with selectivity for copper, silver, cadmium and lead. X-Ray molecular structures of calix[4]arene thioamide–lead(II) and calix[4]arene amide–copper(II) complexes

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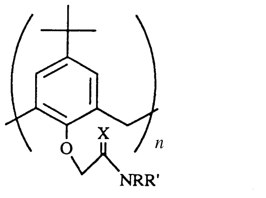
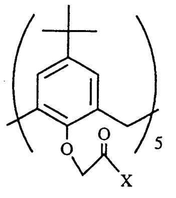
The effect of chemical modification of the lower rim of *p-tert*-butylcalix[4]-, [5]- and [6]-arenes has been analysed with respect to cation binding by thioamide podands. Extraction data for metal picrates from water into dichloromethane are discussed. Cu^{II}, Pb^{II} and Ag^{I} ions are extracted efficiently by all the thioamides studied, whereas extraction of Cd^{II} only reaches significant levels with the pentamer derivative. Unlike their calixarene amide counterparts, these thioamides have no affinity in extraction for either alkali or alkaline earth metals. The X-ray molecular structure of a thioamide–$Pb^{II}(ClO_4)_2$ complex and, for comparison, that of an amide–$Cu^{II}(ClO_4)_2$ complex have been determined. Both complexes exist in the cone conformation with the metal ion encapsulated by the heteroatoms on the lower rin. The crystal structure of the lead complex derivative $5{\cdot}Pb(ClO_4)_2{\cdot}EtOH{\cdot}0.5H_2O$, was solved by Patterson methods and refined by block diagonal least-squares analysis. The crystals are triclinic, space group $P\bar{1}$, $a = 13.394(6)$, $b = 13.459(6)$, $c = 26.711(4)$ Å, $a = 78.33(2)$, $\beta = 87.62(2)$, $\gamma = 60.46(2)°$ with $R = 0.108$ for 4417 observed reflections. The Pb^{2+} is bonded to the four ethereal oxygen and four thiocarbonyl sulfur atoms, [Pb–O, 2.65(2) to 2.72(2), mean value 2.68(3) Å; Pb–S, 2.82(1) to 2.95(1) with a mean of 2.91(3) Å]. The crystal structure of the copper calixarene complex $2{\cdot}Cu(ClO_4)_2{\cdot}H_2O{\cdot}1.4CH_3OH{\cdot}EtOH$, was solved by direct methods and refined by block-diagonal least-squares methods. The crystals are tetragonal, space group *P*4/*ncc* $a = 17.147(2)$, $c = 28.054(4)$ Å, with $R = 0.079$ for 1482 observed reflections. The Cu^{2+} resides on a four-fold axis and is bonded to the four carbonyl oxygen atoms [Cu–O, 1.926(6) Å]. Four ethereal oxygen atoms are at a distance of 2.963(6) Å from the metal ion.

Chemical modification of calixarenes **1**[1,2] on the lower rim represents a simple though effective and versatile way of producing receptors with very selective cation binding properties. We and others have demonstrated complexation of alkali and alkaline cations using calixarenes with pendant ether,[3] ester,[4–9] ketone,[10] carboxylic acid,[11] amide,[12–15] crown ether[16] and hemispherand[17] groups attached to the calixarene substructure through the phenolic oxygen atoms. In some cases the selectivity and strength of complexation were sufficiently favourable to allow the incorporation of the calixarene into ion-selective electrodes[18] and ISFETS,[19] *e.g.* for Na^+ and Cs^+ ion. Alkaline earth salts are strongly bound by calixarene amides, the diethyl amide **1** in the tetramer series exhibiting a large preference in stability constant (*ca.* 10^8) for Ca^{2+} over Mg^{2+} in methanol.[13]



1 $X = O, R = R' = Et, n = 4$
2 $X = O, R = R' = (CH_2)_4, n = 4$
3 $X = O, R = R' = Et, n = 6$
4 $X = O, R = R' = (CH_2)_4, n = 6$
5 $X = S, R = R' = Et, n = 4$
6 $X = S, R = R' = (CH_2), n = 4$
7 $X = S, R = R' = Et, n = 6$
8 $X = S, R = R' = (CH_2)_4, n = 6$
9 $X = O, R = R' = CH_3CH_2CH_2, n = 5$
10 $X = S, R = R' = CH_3CH_2CH_2, n = 5$



11 $X = OH$
12 $X = Cl$

Calixarene ring size is also important with the larger pentamer and hexamer derivatives favouring the larger cations. We have extended our research into chemically modified calixarenes to include systems with binding potential for metallic ions in other regions of the periodic table and we now describe the synthesis and complexation properties of several calixarene thioamides.[20,21]

The availability of several calixarene amides[22] from earlier studies facilitated entry into the thioamide series. Exposure of *p-tert*-butylcalix[4]arene diethyl amide **1**,[14a] its pyrrolidinyl counterpart **2**[13] and their hexamer analogues **3**[14b] and **4**[13] to Lawesson's reagent in hexamethylphosphoric triamide (HMPA) furnished thioamides **5–8**, respectively, in good yield after purification by chromatography over silica gel and recrystallisation. In a similar fashion, *p-tert*-butylcalix[5]arene dipropyl thioamide **10**, chosen to represent the pentamer series, was prepared from its amide counterpart **9**.[23] The ^{1}H NMR spectral data for the two tetramer thioamides **5** and **6** established that both compounds existed in stable cone con-

Table 1 Extraction data (%) for thioamides and, in parentheses, for the corresponding amides[a] thioamide

Cation	5	6	7	8	10
Na^+	7 (95)	4 (91)	5 (27)	5 (49)	—
K^+	8 (74)	6 (58)	7 (23)	5 (52)	—
Mg^{2+}	3 (9)	3 (88)	3 (9)	−(20)	—
Ba^{2+}	3 (74)	2 (67)	7 (86)	3 (94)	—
Co^{2+}	4	4	3	3	—
Cu^{2+}	19 (14)	47 (20)	15	42	38
Pb^{2+}	56 (97)	96 (94)	32	46	64
Cd^{2+}	8 (97)	9 (81)	8	58	42
Ag^+	80 (99)	98 (97)	95 (81)	94 (97)	96
Pr^{3+}	2 (14)	3 (11)	2	—	—

[a] Data and experimental procedure from ref. 13.

formations with singlets for the *tert*-butyl groups and the aromatic protons and AB patterns for the protons of the bridging methylene groups of the macrocycle. A very similar pattern was observed in the ^1H NMR spectrum of the pentamer derivative **10**, confirming that it too possessed the cone conformation. We are not, however, able to draw conclusions concerning the conformational preferences of the two hexamer thioamides **7** and **8** since the ^1H NMR data indicated conformational mobility at room temperature, as had also been found to be the case with their amide precursors.

Extraction studies were conducted by the standard two-phase procedure whereby dilute solutions of each calixarene derivative in dichloromethane were shaken with neutral aqueous metal picrate solutions, following which the equilibrium distribution of the picrate was measured spectrophotometrically.[13] Extraction data, expressed as %E, percentage cation extracted, for thioamides **5**–**8** and **10** for a range of metal picrates and, in parentheses, for the corresponding amides, are collected in Table 1. Of the various trends revealed by the data it is clear that these thioamides, unlike the amides, have very little affinity for alkali, alkaline earth and lanthanide cations in extraction. There is a similarly low affinity for Co^{2+}. The levels of extraction of Ag^+ are uniformly very high across the series and are comparable with those observed with the amides. Cd^{2+} is also extracted, but the levels are very sensitive to thioamide constitution and structure: whereas both tetramers **5** and **6** and diethyl hexamer **7** are essentially indifferent to this cation, it is very efficiently extracted by the pyrrolidinyl hexamer **8** and, to a lesser extent, by the pentamer **10**. Cu^{2+} and Pb^{2+} are extracted by all five thioamides, but here again subtle substituent/ring size effects are evident with both metals. The pyrrolidinyl tetramer **6** shows the highest efficiency with Pb^{2+}; for Cu^{2+} both tetramer and hexamer in the pyrrolidinyl form and the pentamer produce good levels of extraction. In general, the switch from a preference for alkali and alkaline earth cations to heavy and transition metal cations is consistent with the change from a hard oxygen-based binding group to a softer sulfur-based binder, and demonstrates the versatility of calixarenes as selective cation binders in that a very wide range of complexing ability can be achieved and modulated with simple chemical modification and substituent variation.

Despite the substantial body of physicochemical data now available with which to quantify the complexation of cations in solution by calixarene derivatives, there is surprisingly little information on the nature of the complexed state. While there are a number of X-ray molecular structures of lower and upper-rim derivatives, there are few compounds for which there exist thermodynamic data on complexation/extraction ability and X-ray structural data. One such system is diethylamide **2** and its KSCN and KI complexes.[14] Both types of data are also available for alkali complexes of calixcrowns[16] and calixspherands[17] and for the Ag^+ complex of a calix[4]arene tetraether.[24] Molecular mechanics calculations are beginning to provide considerable insight into the influence of solvation on conformational change in calix[4]arene amides and their alkali complexes.[25] In an effort to extend the structural data available for calixarene complexes we have conducted an X-ray crystallographic analysis of the $Pb(ClO_4)_2$ complex of diethyl thioamide **5**. For comparison, particularly for the extent of coordination, we have also determined the crystal and molecular structure of the first copper–amide complex, the $Cu(ClO_4)$ complex of pyrrolidinyl amide **2**.

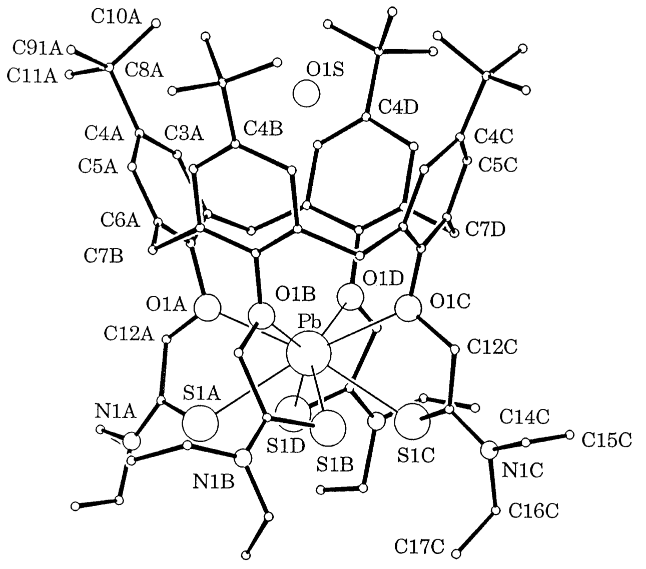


Fig. 1 A view of the Pb–calixarene complex in **5** with an indication of our numbering scheme. Only one orientation of the disordered *tert*-butyl groups is shown.

Although the crystals of **5**·$Pb(ClO_4)_2$, recrystallised from aqueous ethanol, only diffracted relatively poorly (see Experimental section) we were able to obtain sufficient data to determine the details of the conformation unequivocally. The molecule adopts a relatively open distorted cone conformation in the solid state (Fig. 1) and the complexed cation has approximate (non-crystallographic) fourfold symmetry. The Pb^{2+} ion is bonded to four ethereal oxygen and four thiocarbonyl sulfur atoms with Pb–O distances in the range 2.65(2)–2.72(2), mean value 2.68(3) Å, and Pb–S distances in the range 2.82(1)–2.95(1) with a mean of 2.91(3) Å. Only one other Pb-containing calix[4]arene has been reported[26] and it contains Pb in eight-coordination from carbamoylmethoxy O atoms and with Pb–O distances in two groups with mean value 2.61(3) and 2.47(5) Å. In simple thiourea complexes of lead the Pb–S distances are in the range 2.92–3.10 Å.[27] The conformation of **5** in the complex is defined by the angles which the aromatic rings make with the plane through the carbon atoms of the methylene groups which link them, *viz*. 115(1) Å, 109(1)° B, 113(1) °C and 111(1)° D, all rings being tilted so that their *tert*-butyl groups are pitched away from the open cavity. The conformation adopted by the complexed cation creates a cavity which is large enough to accommodate a solvent molecule and this is what we observe. A partial occupancy water molecule is enclathrated within this cavity. Another molecule of solvent is present in the lattice and was allowed for as a disordered ethanol molecule involved in hydrogen bonding with neighbouring perchlorate anions which are also disordered. Important torsion angles in the structure for the O(1*n*)–C(12*n*)–C(13*n*)–S(1*n*) moiety, (n = A, B, C, D) are 0(1)° (A), 17(1)° (B), 14(1)° (C) and 2(1)° (D) and for the Pb–S(1*n*)–C(13*n*)–N(1*n*), 139(3)° (A), 147(4)° (B), 153(3)° (C) and 147(3)°.

The calixarene amide–copper complex, **2**·$Cu(ClO_4)_2$, recrystallised from methanol–dichloromethane, has four-fold crystallographic symmetry and adopts a relatively open conformation with the copper on the four-fold axis (Fig. 2). The metal is bonded to the four carbonyl oxygen atoms (Cu–O,

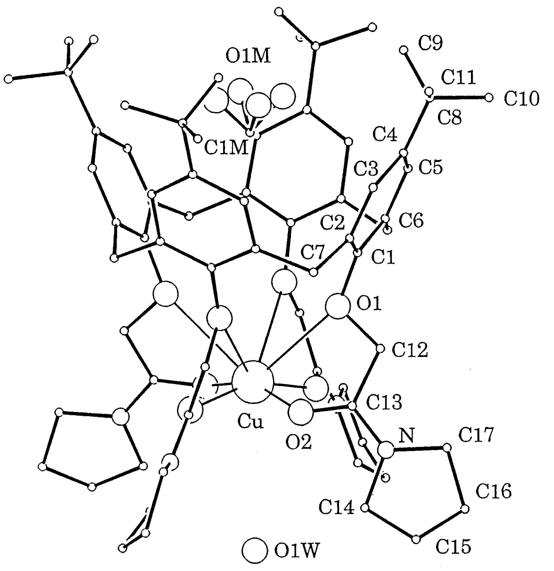


Fig. 2 A view of the Cu–calixarene complex in **2**, with our numbering scheme. The methanol molecule (C1M–O1M) is disordered about the four-fold axis passing through C1M, Cu and O1W.

1.926(6) Å and is at a distance of 2.963(6) Å from the four ethereal oxygen atoms. The position of the copper is such that it is 0.41 Å from the plane of the four ethereal oxygen atoms. The conformation of the complexed macrocycle, as with Pb–thioamide complex, is defined by the angles made by the aromatic rings with the plane through the carbon atoms of the methylene linking groups, all 115.5(5)°. The conformation is thus rather similar to that of its lead analogue in that it creates a cavity at the upper rim large enough to accommodate a solvent molecule. A partial occupancy methanol molecule is enclathrated within this cavity with the carbon atom residing on the four-fold axis and the oxygen disordered about the four-fold axis (Fig. 2) and orientated between the *tert*-butyl groups. There is also a water molecule residing on the four-fold axis in the 'saucer' of the four pyrrolidinyl groups. The water molecule is involved in weak hydrogen bonding with the disordered methanol in the calixarene cavity positioned below it, O · · · O 3.21(6) Å. This hydrogen bonded water–methanol pair is totally enclosed by the macrocycle cavity and the four amide groups of two different calixarenes and extends as a one-dimensional chain through the lattice. The perchlorate anions which reside on two-fold axes are disordered and involved in hydrogen bonding with partial occupancy solvent molecules which were modelled as methanol and ethanol molecules. The volume of the unit cell occupied by the perchlorate anions and solvent molecules is 24% as calculated by the PLATON program.[28] Unlike the Pb complex of thioamide **5**, in which the metal atom is clearly eight-coordinate, the Cu complex of amide **2** has the metal cation in the distorted square-planar environment of the carbonyl oxygen atoms, placing it further away by 1.04 Å from the ethereal oxygen atoms than is the lead cation in the thioamide complex.

These results should facilitate the design and construction of new calixarenes with selective ion-binding properties.

Following the completion of this paper Beer and co-workers[26] have reported the crystal structures of several metal complexes of tetraamide **1**, including the $[Cu{\cdot}\mathbf{1}][ClO_4]_2{\cdot}CH_3CN$ complex.

Experimental

Synthesis of calixarene amides

Tetramer amides **1**[14] and **2**[13] and hexamer amides **3**[14b] and **4**[22] were prepared by published procedures.

***p-tert*-Butylcalix[5]arene dipropyl amide 9.** The known penta-acid **11**[23] (1.0 g, 0.91 mmol) was dissolved in dry benzene (25 cm^3) under nitrogen and oxaloyl chloride (0.79 cm^{-3}, 9.1 mmol) and pyridine (three drops) were added. The solution was stirred at room temp. for 8 h, following which all volatiles were removed at reduced pressure to afford acid chloride **12** as an off-white solid in quantitative yield. The acid chloride was used without further purification. A solution of acid chloride **12** (0.3 g, 0.25 mmol) in dry tetrahydrofuran (THF) (5 cm^3) was added dropwise under nitrogen to a stirred solution of dipropylamine (0.2 cm^3, 1.51 mmol) and triethylamine (0.21 cm^3, 1.51 mmol) in dry THF (10 cm^3). The mixture was stirred for 24 h at room temp., then filtered and the filtrate concentrated to dryness at reduced pressure. The residue was dissolved in dichloromethane and the solution was washed with cold water, dried and concentrated to afford crude **9**. Purification firstly by flash chromatography on neutral alumina using 5% methanol in dichloromethane followed by crystallisation from methanol–dichloromethane yielded **9** as a white solid (0.24 g, 67%), mp 102–103 ° (Found: C, 68.2; H, 9.5; N, 3.5. $C_{95}H_{145}N_5O_{10}{\cdot}2CH_2Cl_2$ requires C, 68.2; H, 9.1; N, 3.9%); ν_{max}(KBr)/cm^{-1} 1658; δ_H($CDCl_3$) 0.90 (30 H, m, CH_3), 1.06 (45 H, s, Bu^t), 1.55–1.59 (20 H, m, CH_2), 3.07 (10 H, t, NCH_2), 3.26–3.30 (15 H, m, NCH_2 and H_B, $ArCH_2Ar$), 4.55 (15 H, s, OCH_2 and d, H_A, $ArCH_2Ar$) and 6.95 (10 H, s, ArH).

General procedure for synthesis of thioamides

To a stirred solution of the calixarene amide in dry HMPA was added Lawesson's reagent (2.1 equiv.). The mixture was stirred at 100 °C under nitrogen for 5 h. The mixture was poured onto ice–water and stirred for 24 h after which the precipitated solid was isolated by filtration, washed with water and dried under vacuum. The solid was then dissolved in dichloromethane and washed again with water. The organic solution was dried and concentrated to afford the crude thioamide which was further purified by flash chromatography on neutral alumina with dichloromethane as eluent followed by recrystallisation from ethanol–dichloromethane. The following thioamides were thus prepared. (Coupling constants are given in Hz).

Thioamide 5. Tetraethylamide **1** furnished thioamide **5** as pale-yellow crystals (69%), mp 92–94 °C (Found: C, 69.6; H, 8.6; N, 4.4; S, 11.3. $C_{68}H_{100}O_4N_4S_4$ requires C, 70.1; H, 8.7; N, 4.8; S, 11.0%); ν_{max}(KBr)/cm^{-1} 1300; δ_H($CDCl_3$) 1.05 (36 H, s, Bu^t), 1.25 (12 H, t, CH_3), 1.30 (12 H, t, CH_3), 3.15 (4 H, d, *J* 11.4, $ArCH_2Ar$), 3.65 (8 H, q, NCH_2), 3.95 (8 H, q, NCH_2), 4.70 (4 H, d, *J* 11.4, $ArCH_2Ar$), 5.10 (8 H, s, OCH_2) and 6.75 (8 H, s, ArH).

Thioamide 6. Tetrapyrrolidinylamide **2** furnished thioamide **6** as pale-yellow crystals (63%), mp 286–287 °C (Found: C, 70.6; H, 8.2; N, 4.9; S, 11.0. $C_{68}H_{92}O_4N_4S_4$ requires C, 70.6; H, 8.0; N, 4.8; S, 11.1%); ν_{max}(KBr)/cm^{-1} 1300; δ_H($CDCl_3$) 1.07 (36 H, s, Bu^t), 1.90 (16 H, m, CH_2), 3.12 (4 H, d, *J* 11.4, $ArCH_2Ar$), 3.50 (8 H, m, NCH_2), 3.82 (8 H, m, NCH_2), 4.90 (4 H, d, *J* 11.4, $ArCH_2Ar$), 5.50 (8 H, s, OCH_2) and 6.75 (8 H, s, ArH).

Thioamide 7. Hexaethylamide **3** furnished thioamide **7** as a pale-yellow solid (42%), mp 128–130 °C (Found: C, 67.3; H, 8.2; N, 4.1; S, 10.1. $C_{102}H_{150}O_6N_6S_6$ requires C, 67.5; H, 8.3; N, 4.6; S, 10.5%), ν_{max}(KBr)/cm^{-1} 1300; δ_H($CDCl_3$) 1.30 (90 H, br m, Bu^t and CH_3), 3.62 (36 H, br m, NCH_2 and $ArCH_2Ar$), 4.75 (12 H, br m, OCH_2) and 7.30 (12 H, br m, ArH).

Thioamide 8. Hexapyrrolidinylamide **4** furnished thioamide **8** as a pale-yellow solid (38%), mp 230 °C (decomp.) (from methanol–dichloromethane) (Found: C, 64.4; H, 7.5; N, 4.5. $C_{102}H_{138}O_6N_6S_6{\cdot}2CH_2Cl_2$ requires C, 65.1; H, 7.5; N, 4.4%); ν_{max}(KBr)/cm^{-1} 1300; δ_H($CDCl_3$) 1.20 (54 H, br m, Bu^t), 2.00 (24 H, br m, CH_2CH_2), 3.75 (36 H, br m, NCH_2 and $ArCH_2Ar$), 4.78 (12 H, br m, OCH_2) and 7.40 (12 H, br m, ArH).

Thioamide 10. Pentamer dipropylamide **9** furnished thioamide **10** as a pale-yellow solid (58%), mp 115–118 °C (Found: C, 71.2; H, 9.0; N, 3.6; S, 10.4. $C_{90}H_{140}N_5O_5S_5$ requires C, 77.4; H, 9.1; N, 4.4; S, 10.0%), ν_{max}(KBr)/cm^{-1} 1290; δ_H($CDCl_3$) 0.95 (30 H, m, CH_3), 1.01 (45 H, s, Bu^t), 1.71–1.85 (20 H, m, CH_2), 3.27 (5 H, d, *J* 13.7, $ArCH_2Ar$), 3.40 (10 H, t, NCH_2), 3.83 (10 H,

Table 2 Summary of data collection, structure solution and refinement details

(*a*) Crystal data		
Empirical formula	$C_{68}H_{100}O_4N_4S_4Pb{\cdot}2(ClO_4)$; $C_2H_5OH{\cdot}0.5H_2O$	$C_{68}H_{92}CuN_4O_8{\cdot}2(ClO_4)$, $1.4CH_3OH$, C_2H_5OH, H_2O
Formula mass	1626.98	1464.90
Colour, habit	Colourless block	Light-green block
Crystal size/mm	0.15 × 0.20 × 0.25	0.25 × 0.35 × 0.70
Crystal system	Triclinic	Tetragonal
a/Å	13.394(3)	17.147(2)
b/Å	13.459(6)	
c/Å	26.711(4)	28.054(4)
α(°)	78.33(2)	
β(°)	87.62(2)	
γ(°)	60.46(2)	
V/Å	4093(2)	8248(2)
Space group	$P\bar{1}$	$P4/ncc$ (No. 130)
Z	2	4
Molecular symmetry	Approx. four-fold	Four-fold
$F(000)$	1686	3121
D_c/g cm^{-3}	1.32	1.17
μ/cm^{-1}	23.0	3.9
(*b*) Data acquisition		
T/ °C	21	21
Unit-cell reflections (2θ-range) (°)	25 (13–37)	25 (18–39)
Max 2θ (°) for reflections	44	48
hkl Range of reflections	−12 14, 0 14, −27 28	0 19, 0 13, 0 31
Decay in standards	25% decay in data collection	10% decay in data collection
Reflections measured	10 178	6241
Unique reflections	9901	3213
R_{int}	—	0.027
Refs with $I > 2\sigma(I)$	4417	1482
Absorption correction type	5 ψ scans	—
Min. max. abs. corr	0.26, 0.60	—
(*c*) Structure solution and refinement		
Solution method	Patterson	Direct methods
H-atom treatment	C-H 0.95 Å, riding	Riding, C-H 0.95 Å; O-H from Δ-map
No. of variables in LS	751	256
k in $w = 1/(\sigma^2 F_0 + kF_0^2)$	0.0012	0.0008
R, R_w, gof	0.108, 0.113, 1.62	0.079, 0.092, 1.43
Density range in final Δ-map/e Å^{-3}	−2.80, 1.80	−0.31, 0.51
Final shift/error ratio	0.06	0.09

t, NCH_2), 4.63 (5 H, d, *J* 13.7, $ArCH_2Ar$), 4.92 (10 H, s, OCH_2) and 6.88 (10 H, s, ArH).

Structure analysis for $2{\cdot}Cu(ClO_4)_2$ and $5{\cdot}Pb(ClO_4)_2$ complexes

Details of the X-ray experimental conditions, cell data, data collection and refinement for the two complexes are summarised in Table 2. Both data collections suffered from intensity loss while the crystals were in the X-ray beam. This was either due to loss of entrapped solvent or radiation damage, or both. The crystals of the **5**·Pb complex diffracted poorly (only 43% of the measured data were labelled 'observed' [$I > 2.0\sigma(I)$, in the 0–20° range] but we were able to obtain sufficient data to allow determination of the conformation unequivocally. The Pb atom was located in the calixarene framework using the Patterson funtion in SHELXS86,[29] and other non-hydrogen atoms were located in successive least squares and difference Fourier maps using the NRCVAX suite of programs.[29] It was obvious at this stage of the refinement that there was considerable disorder in the structure which presented some difficulty in refinement. The *tert*-butyl carbon atoms were each disordered over two orientations. This was allowed for by positioning the 0.5 occupancy carbon sites at geometrically idealised positions C−C 1.50 Å and only refining their thermal parameters isotropically. The corresponding *tert*-butyl hydrogen atoms were also positioned on geometric grounds and included in the structure factor calculations with C−H 0.95 Å. The perchlorate anions were also located; one with its oxygen atoms having high thermal parameters but not disordered; the other was badly disordered and these oxygen atoms were treated by including them in the structure factor calculations at the positions obtained from difference maps (their thermal parameters allowed only isotropic refinement). A disordered ethanol of solvation was also located in the lattice but no hydrogen atoms were positioned on this molecule. All other hydrogen atoms (visible in difference maps at an intermediate stage of refinement) were included at geometrically idealised positions, but restrained to ride on the carbon atom to which they were bonded (C−H 0.95 Å). The final refinement cycles were by block-diagonal least-squares and gave a final R, R_w and GoF of 0.108, 0.113 and 1.62, respectively (with a data to parameter ratio of 5.9 : 1).[30]

The crystals of **2**·$Cu(ClO_4)_2$ were air sensitive and were mounted quickly on a glass fibre in epoxy cement. The Cu atom was located in the calixarene framework using direct methods and the other non-hydrogen atoms were located in successive least squares and difference Fourier maps using the NRCVAX suite of programs. As with the Pb complex, it was obvious at this stage of refinement that there was considerable disorder in the structure, presenting some difficulties in refinement. Although the *tert*-butyl carbon atoms had high thermal parameters, there was no indication that there was a minor component present in a second orientation. The disordered methanol molecule enclathrated in the calixarene cavity was located and the oxygen atom, which was disordered about the four-fold axis was given 25% occupancy. The perchlorate anions were located on two-fold axes and were disordered; the partial oxygen atom sites had high thermal parameters. A disordered partial occupancy method and ethanol of solvation were also located in the lattice near the perchlorate anions and were refined isotropically (no hydrogen atoms were positioned on either molecule). All other

Table 3

(*a*) Summary of selected bond lengths (Å) for $Pb(ClO_4)_2$ complex of **5**

Pb–O (1A)	2.662(18)
Pb–O (1B)	2.719(19)
Pb–O (1C)	2.646(18)
Pb–O (1D)	2.692(21)
Pb–S (1A)	2.913(9)
Pb–S (1B)	2.951(11)
Pb–S (1C)	2.824(10)
Pb–S (1D)	2.936(10)

cis angles involving oxygen
O–Pb–O *cis* angles in range 79.5(6)–83.9(6)°
S–Pb–S *cis* angles in range 72.3(3)–75.7(7)

(*b*) Summary of selected bond lengths (Å) for the $Cu(ClO_4)_2$ complex of **2**

Cu–O2	1.926(6)
Cu···O1	2.963(6)
O–Cu–O	*cis* angle 87.4(3)°

hydrogen atoms (visible in difference maps at an intermediate stage of refinement) were included at geometrically idealised positions, but restrained to ride on the carbon atom to which they were bonded (C–H 0.95 Å); the disordered water hydrogen atoms were located from difference maps and included at these positions in the structure factor calculations. The final refinement cycles were by block-diagonal least-squares analysis and gave a final R, R_w and GoF of 0.079, 0.092 and 1.43, respectively, (with a data to parameter ratio of 5.8:1) using the NRCVAX suite of programs. The figures were prepared with the aid of ORTEPII[31] and PLUTON.[32] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/53. Copies of the structure factor listings are available from the authors.

References

1 C. D. Gutsche, *Calixarenes*, vol. 1 in 'Monographs in Supramolecular Chemistry', ed. J. F. Stoddart, Royal Society of Chemistry, Cambridge, 1989.

2 *Topics in Inclusion Phenomena*, *Calixarenes a Verstaile Class of Macrocyclic Compounds*, ed. V. Böhmer and J. Vicens, Kluwer Academic Publishers, 1990.

3 V. Bocchi, D. Foina, A. Pochini, R. Ungaro and C. D. Andreetti, *Tetrahedron*, 1982, **38**, 373.

4 M. A. McKervey, E. M. Seward, G. Ferguson, B. L. Ruhl and S. J. Harris, *J. Chem. Soc., Chem. Commun.*, 1985, 388.

5 S. K. Chang and I. Cho, *Chem. Lett.*, 1984, 477; *J. Chem. Soc., Perkin Trans. 1*, 1986, 211.

6 M. J. Schwing-Weill and M. A. McKervey, ref. 2, pp. 149–172.

7 F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marquis, B. L. Ruhl, M. J. Schwing-Weill and E. M. Seward, *J. Am. Chem. Soc.*, 1989, **111**, 8681.

8 A. Arduini, A. Pochini, S. Reverberi, R. Ungaro, G. D. Andreetti and F. Ugozzoli, *Tetrahedron*, 1986, **42**, 2089.

9 F. Arnaud-Neu, G. Barrett, S. Cremin, M. Deasy, G. Ferguson, S. J. Harris, A. J. Lough, L. Guerra, M. A. McKervey, M. J. Schwing-Weill and P. Schwinte, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1119.

10 G. Ferguson, B. Kaitner, M. A. McKervey and E. M. Seward, *J. Chem. Soc., Chem. Commun.*, 1987, 584.

11 F. Arnaud-Neu, G. Barrett, S. J. Harris, M. A. McKervey, M. Owens, M.-J. Schwing-Weill and P. Schwinte, *Inorg. Chem.*, 1993, **32**, 2644.

12 G. Calestani, F. Ugozzoli, A. Arduini, E. Ghidini and R. Ungaro, *J. Chem. Soc., Chem. Commun.*, 1987, 344.

13 F. Arnaud-Neu, M.-J. Schwing-Weill, K. Ziat, S. Cremin, S. J. Harris and M. A. McKervey, *New. J. Chem.*, 1991, **15**, 33.

14 (*a*) A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, G. D. Andreetti, G. Calestani and F. Ugozzoli, *J. Inclusion Phenom.*, 1988, 119; (*b*) G. D. Andreetti, G. Calestani, F. Ugozzoli, A. Arduini, E. Ghidini, A. Pochini and R. Ungaro, *J. Inclusion Phenom.*, 1987, **5**, 123; (*c*) very recently the X-ray crystal structure of a strontium complex of diethyl amide **2** was published, N. Muzet, G. Wipff, A. Casnati, L. Domiano, R. Ungaro and F. Ugozzoli, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1065.

15 S. K. Chang and I. Cho, *Chem. Lett.*, 1987, 947.

16 R. Ungaro and A. Pochini, ref. 2, pp. 127–147; C. Alfieri, E. Dradi, A. Pochini, R. Ungaro and G. D. Andreetti, *J. Chem. Soc., Chem. Commun.*, 1983, 1075; E. Ghidini, F. Ugozzoli, R. Ungaro, S. Harkema, A. Abu El-Fadl and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1990, **112**, 6979.

17 D. N. Reinhoudt, P. J. Dijkstra, P. J. A. in't Veld, K. E. Bugge, S. Harkema, R. Ungaro and E. Ghidini, *J. Am. Chem. Soc.*, 1987, **109**, 4761.

18 D. Diamond, G. Svehla, E. Seaward and M. A. McKervey, *Anal. Chim. Acta*, 1988, **204**, 223; K. Kumura, M. Matsuo and T. Shona, *Chem. Lett.*, 1988, 615.

19 J. A. J. Brunick, J. R. Haak, J. G. Bomer, D. Reinhoudt, M. A. McKervey and S. J. Harris, *Anal. Chim. Acta*, 1991, **254**, 75; R. J. W. Lugtemberg, Z. Brzozka, A. Casnati, R. Ungaro, J. F. J. Engbersen and D. N. Reinhoudt, *Anal. Chim. Acta*, 1995, **310**, 263.

20 For a preliminary report of this work, excluding the X-ray crystal structures, see F. Arnaud-Neu, M. A. McKervey and M.-J. Schwing-Weill, *J. Phys. Org. Chem.*, 1992, **5**, 496. Shortly after this report, the use of calixarene derivatives, including thioamides as ionophores in ESFET devices, was described by P. L. H. M. Cobben, R. J. M. Egberink, J. G. Bomer, P. Bergveld, W. Verboom and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1992, **114**, 10573.

21 S. J. Harris, M. McManus, C. McArdle and M. A. McKervey, *Eur. Pat. No.* 0432989A2, 12 December 1990.

22 F. Arnaud-Neu, G. Barrett, S. Fanni, D. Marrs, W. McGregor, M. A. McKervey, M.-J. Schwing-Weill, V. Vetrogon and S. Wechsler, *J. Chem. Soc., Perkin Trans 2*, 1995, 453.

23 For the preparation of the carboxylic acid from which this amide was made, see G. Barrett, M. A. McKervey, J. F. Malone, A. Walker, F. Arnaud-Neu, L. Guerra, M.-J. Schwing-Weill, C. D. Gutsche and D. R. Stewart, *J. Chem. Soc., Perkin Trans 2*, 1993, 1475.

24 A. Ikeda and S. Shinkai, *J. Am. Chem. Soc.*, 1994, **116**, 3102.

25 P. Guilbaud, A. Varnek and G. Wipff, *J. Am. Chem. Soc.*, 1993, **115**, 8289; A. Varnek and G. Wipff, *J. Phys. Chem.*, 1993, **97**, 10840.

26 P. D. Beer, M. G. B. Drew, P. B. Leeson and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1995, 1273.

27 M. Nardelli and G. Fava, *Acta Crystallogr.*, 1959, **12**, 727.

28 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.

29 G. M. Sheldrick, SHELXS86, Crystallographic Computing 3, G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, London, 1986, pp 175–189.

30 E. J. Gabe, Y. Lepage, J. P. Charland, F. L. Lee and P. S. White, *J. Appl. Cryst.*, 1989, **22**, 384.

31 C. K. Johnson, ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA 1976.

32 A. L. Spek, PLUTON Molecular Graphics Program, The University of Utrecht, The Netherlands, 1991.

Paper 6/05417J
Received 2*nd August* 1996
Accepted 10*th October* 1996