Systematic Structural Coordination Chemistry of *p-tert*-Butyltetrathiacalix[4]arene: Main Group Metal Complexes Other Than Those of Group 1[‡]

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In extension of previous work involving structural characterisation of complex salts formed between main group 1 metal ions and *p-tert*-butyltetrathiacalixarene, LH_4, the present study encompasses complexes with a wider array of main group 2, 13, 14 metal ions. For group 2, single-crystal X-ray structural characterisation of $Ca(LH_3)_2 \cdot 3dmf$ (**1a**), $\{Ca(LH_2) \cdot 3dmf\}_2$ (**1b**), $Ba(LH_3)_2 \cdot 6dmf$ (**2a**) and $BaCO_3 \cdot 3Ba(LH_3)_2 \cdot 3H_2O \cdot 3CH_3CN \cdot 12.25CH_2Cl_2$ (**2b**) provides models for various coordination units. For group 13, this applies to $\{Ga(OH)-$ $(LH_2) \cdot 3.5dmf\}_2$ (**3**), $\{In(LH) \cdot 4EtOH \cdot 2CH_2Cl_2\}_2$ (**4a**) and $\{In(OH)(LH_2) \cdot 3CH_2Cl_2\}_4$ (**4b**), and for group 14, to $OPb_4(LH)_2 \cdot$ $6dmf \cdot dmso \cdot 2H_2O$ (**5**). Overall, these define mononuclear (**1a**, **2a**), binuclear (**1b**, **3**, **4b**) and tetranuclear (**2b**, **4b**, **5**) species. The calixarene cavities frequently include solvent molecules, though this capacity is clearly influenced by the nature of the bound metal ion(s) and their binding, as well as the associated impact on the conformation of the calixarene ligand(s).

Introduction

Macrocyclic ligand chemistry[1] may be considered emblematic of the development of much coordination chemistry in the second half of the twentieth century and the large group[2] of methylene-bridged cyclo-oligomers of *p*-substituted phenols known as "calixarenes"[3] has a well-established chemistry which includes many applications in the area of metal ion coordination.[3–16] As synthetic macrocyclic ligands, the calixarenes are somewhat unusual in that the donor sites for metal ion binding are most commonly atoms within pendent substituents rather than within the macrocycle itself. There are parallels here with some naturally occurring "ionophores"[17] but only the relatively recent synthesis of calixarene systems in which sulfur replaces the methylene groups, those of the thiacalixarenes[18–21] (as well as mercaptothiacalixarenes[22,23] and thiacalixanilines[24,25]), has provided materials which may be considered comparable to a wide range of macrocycles, both natural (e.g. the porphyrins[26]) and synthetic,[1] in which macro-

cyclic ring atoms may be donors. Nonetheless, there are reasons to believe that the thiacalixarenes and their derivatives may constitute a rather unique class of macrocycles[21,27] with unusual metal-binding properties.[2–16,28–46]

A common feature of known calixarene and thiacalixarene chemistry is the formation of inclusion complexes,[3,4,23,27,37,47,48] and this, of course, may be considered as another form of "coordination" chemistry,[49] though the exact forces at work are difficult to identify and quantify,[47] especially as most precise data derive from solid-state structural determinations where both inter- and intra-molecular interactions may be involved.[47,50] Comparison in particular of *p-tert*-butyltetrathiacalix[4]arene (Figure 1) and *p-tert*-butylcalix[4]arene in their *cone* forms, however, does indicate that the slightly larger size of the thiacalixarene cavity may give rise to significantly different inclusion proclivities and that these may be modified by simultaneous metal ion coordination.[37a] In all known cases other than those of the uranyl and zirconium(IV) complexes,[38] metal ion coordination to *p-tert*-butyltetrathiacalix[4]arene involves binding to the sulfur atoms of the macrocycle as well as to the pendent phenoxide-*O* atoms. To further explore the interaction of coordination and inclusion, and to broaden the perspectives for metal-ion binding by thiacalixarenes, we embarked upon efforts to characterise, by X-ray crystallographic studies, as wide a range of metal complexes of *p-tert*-butyltetrathiacalix[4]arene as possible. Such work is completely dependent upon the ability to obtain suitably crystalline materials and, although the synthesis of thiacalixarene complexes is frequently trivial, their conversion to

crystals of an appropriate nature is, in our experience,[30,36–39,42–44] subtly dependent upon both equilibrium and kinetic factors, although it does appear that solvothermal methods may provide more readily reproducible means of obtaining crystalline thiacalixarene complexes.[46] Thus, the present and two following reports are restricted to the description of a range of structures somewhat more limited than initially envisaged, most probably only indicative of possible forms for thiacalixarene complexes rather than any equilibrium preferences. A number of intriguing features are nonetheless apparent in the results available, this paper expanding upon known studies of main group 1 cation complexes of both the partly deprotonated thiacalixarene (Part I)[37] and its fully deprotonated form,[51] to encompass further adducts with ions of main groups 2, 13 and 14, for which no structurally defined examples are yet known. In the present and its associated works concerned with transition metal[52] and lanthanide(III)[53] cation complexes, inclusion of a solvent molecule within a calixarene cavity is designated by the use of a large dot, "·", the parent fully protonated neutral ligand (Figure 1) being LH$_4$.
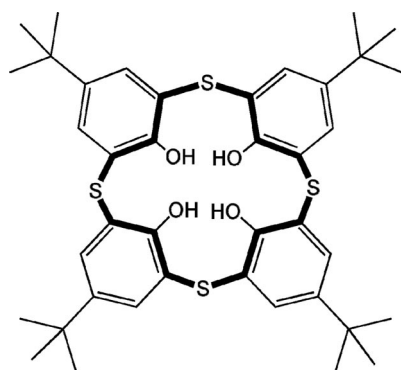

Figure 1. A representation of *p-tert*-butyltetrathiacalix[4]arene, LH$_4$, with the bonds constituting the macrocyclic ring shown bold; actual structures of the *cone* form of the unsolvated and solvated molecule are given in ref.[37a]

Results and Discussion

It is essential to recognise that the present work concerns the solid state coordination chemistry of *p-tert*-butyltetrathiacalix[4]arene and that the related solution chemistry remains to be defined, though it is assumed that the solid-state structures represent useful indicators of at least some of the forms possible for solution species. With the intent that sufficient metal to replace all calixarene protons would be present, a ratio of metal reactant to thiacalixarene of 2:1 was used. Unsurprisingly, the metal/ligand ratio in the complexes precipitated was often different and it is presumed that many of the syntheses presently reported could be modified to improve at least the atom efficiency with respect to both metal and thiacalixarene. No doubt also triethylamine in excess could be substituted by bases enabling more specific degrees of thiacalixarene deprotonation to be achieved. Nonetheless, it is clear from the sensi-

tivity of many systems to seemingly minor variations in procedure, that optimisation of all syntheses might be an extremely extended investigation involving the exploration of both kinetic and thermodynamic factors influencing product crystallisation. The water content of the solvents used [dimethyl sulfoxide (dmso), dimethylformamide (dmf), acetonitrile, dichloromethane, ethanol] was presumably important in the generation of species found crystallographically to incorporate water, hydroxide and/or oxide, and deliberate addition of approximately stoichiometric amounts of water to the initial reaction mixtures did accelerate the rate of deposition of such products.

In terms of the Periodic Table it is logical to resume description of the structures of *p-tert*-butyltetrathiacalix[4]arene complexes at a point adjacent to that of the metal group, the alkali metals (group 1), most completely studied to date.[37,51] It is also appropriate in that the alkaline earth metal calcium forms complexes of relatively simple nature, including one rather similar in some respects to that of its neighbour, potassium, so that this system is a convenient one through which to identify some issues of general importance. (For group 2 in particular, considerable effort was expended in attempting to provide characterisation as complete as that of group 1 but crystals appropriate for structure determinations were obtained with Ca and Ba complexes only.) The study of calcium complexation firstly demonstrates that quite different species may crystallise from reaction mixtures of only slightly different overall composition. Thus, an error in calculating required reagent quantities during the first attempt to obtain the Ca^{II} complex resulted in a reaction mixture in which the Ca/thiacalixarene ratio was 1.5:1 and from which a Ca(thiacalixarene)$_2$ species crystallised. When the synthesis was repeated with the ratio adjusted to the desired value of 2:1, a Ca$_2$(thiacalixarene)$_2$ species precipitated. Because neither solid has the stoichiometry of the reaction mixture, presumably these results reflect the occurrence of multiple complexation equilibria in the solution phase, though it is not presently possible to completely exclude the possibility that the nature of the precipitated solids was determined by crystallisation kinetics.

The results of the single-crystal X-ray structure determinations are consistent with the stoichiometries and connectivities as given below, albeit in some cases protonic hydrogen atom locations are less certain than desired, in consequence of precision limited by disorder, large peripheral displacement parameters (etc.). We discuss the structures individually initially in terms of metal and in order of increasing complexity within each metal where appropriate. In each of the present triad of papers, a summary of ligand conformational and geometrical descriptors is presented in Tables S1 and S2 (Supporting Information), which also give adjacent phenolic O···O distances assisting assignment of putative or definitive (by refinement) associated hydrogen atom locations, the distance tending to be short when containing a protonic hydrogen atom, and long when chelating a metal atom (the two situations usually mutually exclusive). [In a number of bis(ligand) situations, interligand

O⋯O distances are also less than 3 Å but at this point there is no evidence to support proton localisation between pairs of ligands.] Metal-atom deviations from the $C_6(O)$ planes, and interplanar dihedral angles between the aromatic ring and O_4 planes (indicative of *cone* pitch and distortion) are also given. Atom deviations δ(O,M) from the O_4 planes are given, also δS, the latter in a number of cases showing surprising variations despite relatively constant (angular) geometries about the sulfur atoms and, often, essentially planar O_4 arrays. Metal atom coordination environments are presented in the subsequent Tables (Supporting Information), with selected parameters accompanying the figures.

$Ca(LH_3)_2$·3dmf ≡ [(dmf-*O*)$_2$Ca(H$_3$L)(H$_3$L·dmf)] (1a)

The stoichiometric/molecular unit present in the crystal lattice is shown in Figure 2; the metal-atom environment is given in Table S3 with ligand descriptors in Table S1 (Supporting Information). Its form, with a metal-containing unit held between two calixarene ligands, is one commonly but not universally found in known thiacalixarene complexes.[20,30,37–46] Here, one mononuclear formula unit, devoid of crystallographic symmetry, comprises the asymmet-

ric unit of the structure, in which the two calixarene entities adopt *cone* conformations of near-fourfold symmetry (Table S1) and, phenolic hydrogen atoms having been refined, both appear to be singly deprotonated. Phenolic oxygen atoms O(111,131,141;221,231,241) are assigned as protonated on the basis of refinement of associated $(x,y,z,U_{iso})_H$; in general H(*mnl*) are hydrogen-bonded to O[*m*(*n* – *1*)*1*]. Both ligands function only as tridentate, OSO donor species (with one of these two *O*-donors being the formally negative phenoxide-*O* in each case, so that the coordination is unsymmetrical); the coordination environment of the calcium atom is irregular eight-coordinate [Table S3, (a)], made up of contacts from two adjacent ("chelating") pairs of phenoxide oxygen atoms *plus* their in-between sulfur atoms completing *fac*-OSO tripods (the unsymmetrical metal–oxygen distances being reflected in their associated M–O–C angles) and with other adjacent sulfur atoms at longer distances. Two of the three dmf molecules (#2,3) are coordinated, the third (#1) being contained within the cavity of ligand 2. The dmf and phenoxide-*O* donors are tightly bound (Ca–O < 2.35 Å), the hydroxy-*O* of the ligand less so (Table S3, Figure 2).

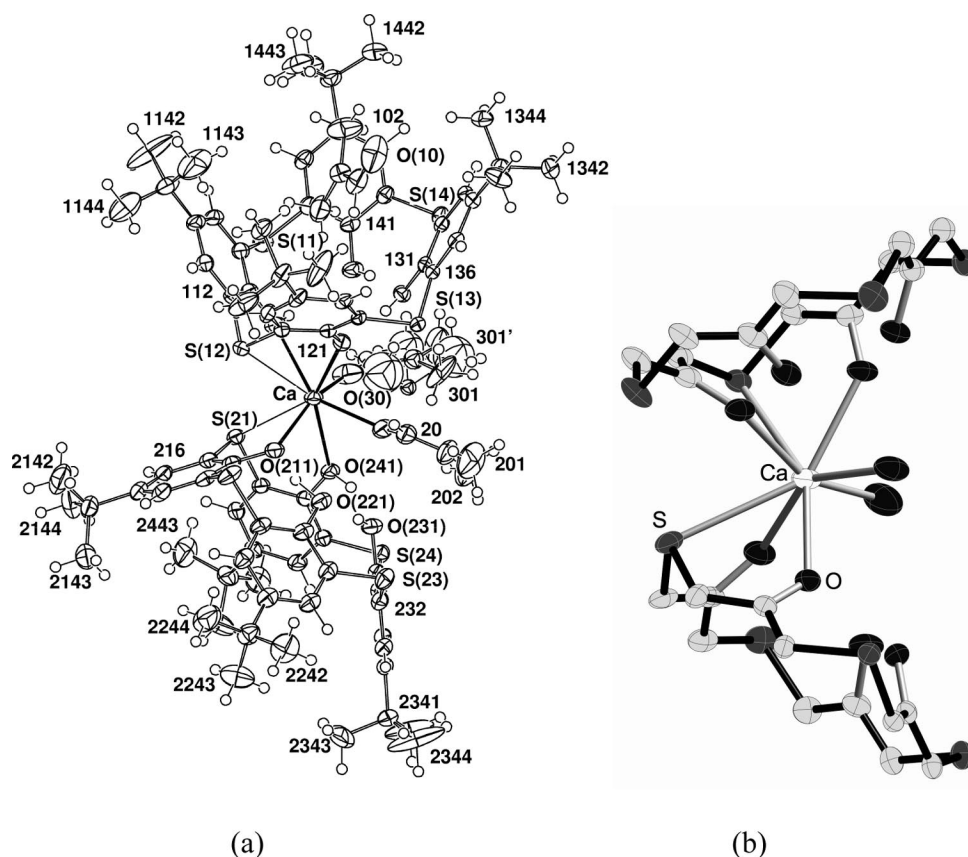In each ligand, the three O⋯O distances assigned as containing a hydrogen bond are shorter than the fourth, that

Figure 2. (a) Projection of the "molecular" array of [(dmf-*O*)$_2$Ca(H$_3$L)(H$_3$L·dmf)] (**1a**). Ca–O(20,30) (dmf) are 2.353(3), 2.287(3) Å. Within the OSO tripods, Ca–S(12,21); O(111,121,211,241) are 3.114(1), 2.973(1); 2.621(2), 2.287(2), 2.345(2), 2.485(2) Å. Dmf is included in ligand 1. (b) Simplified, perspective view of the coordination core of **1a**, with only the macrocyclic ring atoms and oxygen substituents of the calixarene shown. (To better define the macrocycle, bonds within it are shown black. *O*- and *S*-donor atoms are shown in different shades of grey, as indicated by the labelling.)

last pair being the one which chelates the metal atom (see above). Despite six of the eight ArO groups not being coordinated, their C–O bonds are directed toward the calcium atom so that it lies no more than 1.836(9) Å out of any phenolic C_6 plane; the pitch of the C_6 plane to the associated O_4 plane is greatest for the deprotonated ArO in each ligand (Table S1). The calixarene ligands are inequivalent, differing not only quite significantly in the donor atom distances from the calcium atom (Table S3) but also in that only one includes a molecule of dmf, the methyl component directed within the cavity. The other cavity is filled as a result of "hermaphrodite pair" formation,[37a] involving the mutual interpenetration of *tert*-butyl and cavity components of calixarene entities associated with separate calcium atoms (and presumed to be associated with $CH_3 \cdots \pi$ interactions[54]). Unlike the potassium complex, where such interactions lead to polymerisation,[37a] the presence of dmf means that one way to regard the lattice of the calcium complex **1a** is as if it were made up from $[(dmf \cdot LH_3)(dmf-O)_2Ca(H_3L \cdot LH_3)Ca(O-dmf)_2(H_3L \cdot dmf)]$ "dimers". The $Ca \cdots Ca$ separation [16.425(1) Å] in this unit, nonetheless, is not the shortest found in the lattice, a separation of 11.258(1) Å being found for a side-by-side arrangement of the dimers in which *tert*-butyl groups come within van der Waals contact distances as well as approaching "externally" aromatic carbon atoms. In addition, the dmf-filled calixarene cavities confront one another in such a way that the associated Ca atoms are 19.235(1) Å apart. This centrosymmetric confrontation involves some $CH_3 \cdots CH_3$ separations <4 Å and dmf-$O \cdots CH_3$ contacts ca. 3.5 Å. The coordination geometry of the calcium atom is very irregular and the $Ca \cdots S$ separations [2.973(1), 3.114(1) Å] are long and presumably indicative of weak interactions, though certainly the sulfur atoms lie in space which would otherwise have to be considered as defining a remarkable coordination sphere vacancy. The observation of association by inclusion in the present structure offers some justification for regarding the $Ca(LH_3)_2$ unit as a "molecular tecton",[55] i.e. here as a unit which, by cavity inclusion, may serve to form part of a multidimensional network, and in this regard it can be considered as a "bent connector". Given the variety of coordination modes known for Ca^{II},[56] however, it is probably unrealistic to assume that it would be a connector of significant rigidity. Given also that the formally uncoordinated phenolic OH groups of the calixarene lie within hydrogen-bonding distances of the coordinated dmf oxygen atoms, it is possible that the bent form of the $Ca(LH_3)_2$ unit is a particular consequence of the presence of ligated dmf. The adjacent coordination of these ligands may be indicative of attractive interactions between them also.[57] There is nothing to indicate that *p-tert*-butyltetrathiacalix[4]arene is an especially effective ligand for Ca^{II}, the involvement of the macrocycle-S atoms in binding not leading to any marked enhancement of $Ca \cdots O$ interactions when compared with those in a simple calixarene system.[58] This is a conclusion of some relevance to understanding the form of the mixed Pd/Ca complexes of the thiacalixarene, discussed in an associated paper.[52]

$CaLH_2 \cdot 3dmf$ (×2) $\equiv [\{(dmf-O)_2Ca\}_2\{\mu-O,O',O''-(H_2L \cdot dmf)\}_2]$ (1b)
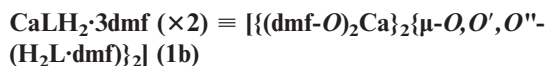
Here, one binuclear formula unit comprises the asymmetric unit of the structure. Although devoid of crystallographic symmetry, the array has quasi-*m* symmetry, the quasi-mirror plane passing through the bisector of the line between the pair of calcium atoms [separation: 3.555(3) Å] and through the phenoxy-*O* bridges, one from each ligand (Figure 3). Each ligand cavity contains a dmf molecule. Most basic features of the structure of this complex (Figure 3) are very similar to those of **1a**, augmented by the insertion of a further $Ca(O-dmf)_2$ unit. The essentially equivalent coordination spheres of the two calcium atoms are irregular eight-coordinate [Table S3, (b)], each comprising a bridging phenoxide-O from each ligand, one of the phenoxy-*O* groups to either side of the latter, bound terminally, and a pair of terminally bound *O*-dmf ligands. As well, in each case, the sulfur atom between the pair of bound phenoxy-*O* interactions of each ligand lies close to the calcium atom at a distance similar to those noted as "bonding" in complex **1a** (Table S3), implying comparable interactions. Each ligand binds here, therefore, as a pair of unsymmetrical OS(O-μ) *fac*-tripods (μ-O common).

While hydroxo-*H* atoms have not been located, almost certainly one of the deprotonated phenoxide groups provides the bridging O(n11) atom of each ligand, the $O(n11) \cdots O(n21)$ distances being large (Table S1) and accommodative of the interacting sulfur atoms, the more remote pair of these being associated with Ca(1), reflecting rather large disparities in the two coordination environments, and breaking any putative *m*-symmetry, though not with any systematic effect on the associated C–S–C angles (Table S2). Presumably one of the other chelating phenoxy group components, perhaps that with the shorter Ca–O distance, is deprotonated in each ligand; the more distant $O \cdots O$ pairs are adjacent in each O_4 grouping, as also are the shorter pairs which are presumably bridged by H^+. The crystal packing in both complexes **1a** and **1b** may be considered as layered, normal to the *bc* diagonal in **1a**, and normal to *b* or the *bc* diagonal in **1b**. Here, attractive formyl-*C* ··· formyl-*O* interactions (indicated by atom approaches ca. 3.1 Å) may influence the disposition of the dmf ligands about the metal atoms, which in this system is seemingly not influenced by hydrogen-bonding to phenol units. Both macrocycles are in conformations close to that of a regular *cone*, with only partial coordination of their full set (O_4S_4) of donor atoms, both factors perhaps once more indicating that the Ca^{II}–calixarene interaction is not particularly strong.

In contrast to **1a**, the binuclear species of **1b** involves phenoxide donor bridging and this is achieved in such a way that each calixarene ligand is quinquedentate (O_3S_2) [double OS(O-μ)] *fac*-tripod, common (μ-O) towards the dicalcium unit but with rather different atom separations (Tables S1, S3). One oxygen atom and its two adjacent sulfur atoms appear to be uncoordinated in both, a situation which may be dependent upon the different formal charge
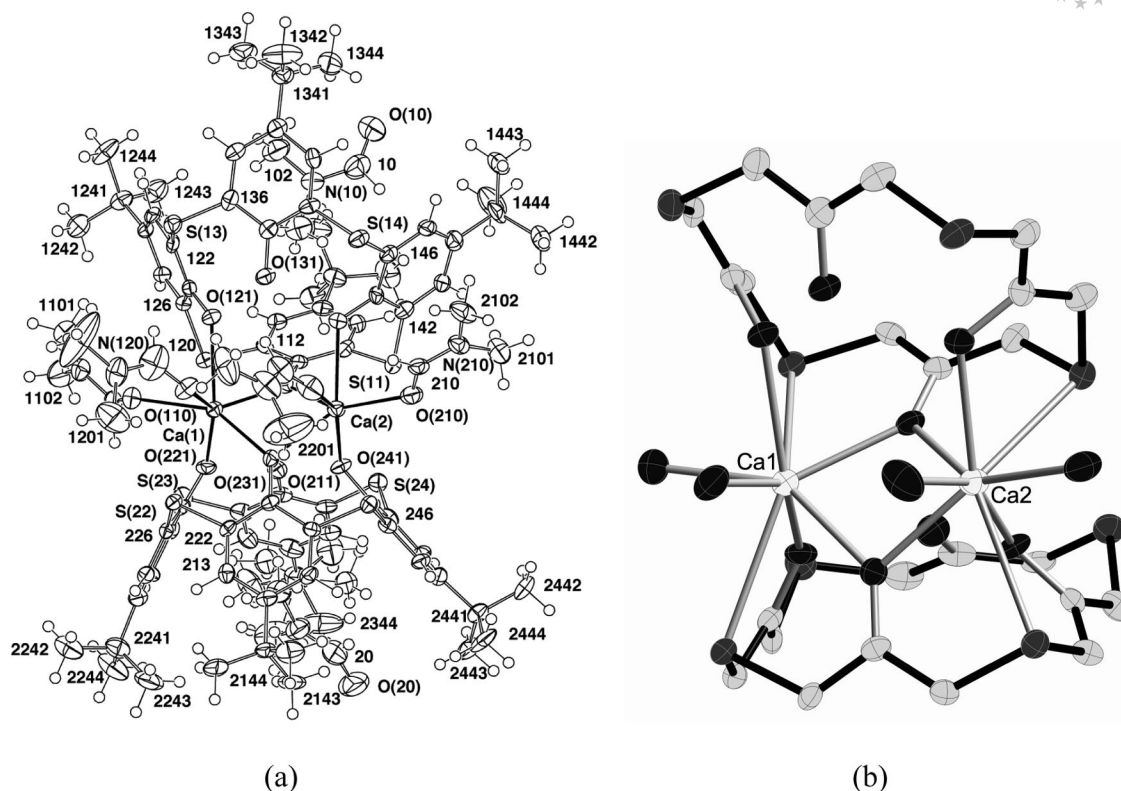
Figure 3. (a) Projection of the binuclear array of [{(dmf-*O*)$_2$Ca}$_2${μ-*O*,*O*′,*O*″-(H$_2$L·dmf)}$_2$] (**1b**), with the quasi-mirror plane approximately coplanar with the page. Ca–O(dmf) are 2.328(10)–2.400(9) Å. Within the OS(O-μ) tripods, Ca–O(μ) are 2.340(8)–2.373(8), Ca–O(outer) 2.310(7)–2.619(7), Ca–S 2.917(4)–3.056(4) Å. Ca···Ca is 3.555(3) Å. (b) Simplified perspective view of the coordination core of the dimer, with only the macrocyclic ring atoms and their oxygen substituents of the calixarene shown.

carried by the calixarenes in the binuclear complex. Although **1b** is formulated above as a species involving a pair of doubly deprotonated calixarene units, with phenolic hydrogen atoms not being located in the structure solution, an alternative formulation could be as [{(dmf-*O*)$_2$Ca}$_2$-(HL·dmf)(H$_3$L·dmf)]. In addition to some disparity in their calcium interaction distances [Ca(1)–O(121) is curiously long, 2.619(7) Å], the two calixarene units do differ in that the uncoordinated oxygen atom of one [O(231)] is within hydrogen-bonding distance [3.168(10) Å] of the bridging phenoxide (phenol)-*O* [O(111)] derived from the other, as well as of the adjacent oxygen atoms of its own macrocycle, whereas the uncoordinated oxygen atom of the other is only within hydrogen-bonding distance of its adjacent phenoxo(phenol) oxygen atoms. Such slight differences between the two calixarene units may be partly masked by the difference from **1a** in that both calixarene cavities are now occupied by dmf molecules. Obviously, this excludes hermaphroditic association in the lattice, though there is a partial confrontation of dmf-filled cavities which, as in the mononuclear complex, may be due to weak CH···O and CH$_3$···CH$_3$ attractions. The binuclear complex may again be regarded as a bent, ditopic receptor, though one of different dimension in terms of the separation of the cavities.

Ba(LH$_3$)$_2$·6dmf ≡ [(dmf-*O*)$_4$Ba(H$_3$L·dmf)$_2$] (2a)

Under similar preparative conditions in dmf as solvent, Ba^{II}, like Ca^{II}, provided a crystalline precipitate of a 1:2 M/

L stoichiometry, quite different to that of the solution. One mononuclear formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The coordination environment about the barium has quasi-*2* symmetry; the intervening sulfur atoms also may again be considered to interact as shown in Figure 4, so that the ligands again bind as OSO *fac*-tripods, this time remarkably symmetrically [Table S4, (a)]. The longer bonds and higher coordination number expected for Ba^{II} relative to Ca$^{II[59]}$ are presumably some of the factors causing this complex to adopt a structure (Figure 4) better described as derived from a "stepped" and not bent, ditopic receptor. As in the ligands of the calcium compounds (Table S1), the chelating *O*,*O*′ pairs have the longest *O*···*O*′ distances within the O$_4$ sequences; presumably one of the oxygen atoms of each of these pairs is deprotonated. Although the Ba···O distances do not differ significantly within each pair, the O···O distances to either side do, suggesting O(121,241) to be the deprotonated oxygen atoms. The four dmf-*O* donor atoms O(30–60) form a puckered plane about the barium centre [δO –0.26, 0.28, 0.32, 0.26(1); δBa 0.0907(1) Å]. Each ligand cavity contains an uncoordinated dmf molecule and both calixarenes have close to *cone* conformations. Confrontation of the cavities leads to the formation of columns parallel to *b*, the included dmf molecules being involved in close CH···O approaches to the *tert*-butyl methyl groups of the adjacent molecule, with some close CH$_3$···CH$_3$ contacts (<4 Å) also apparent. The Ba···Ba separation within these

(a)   (b)
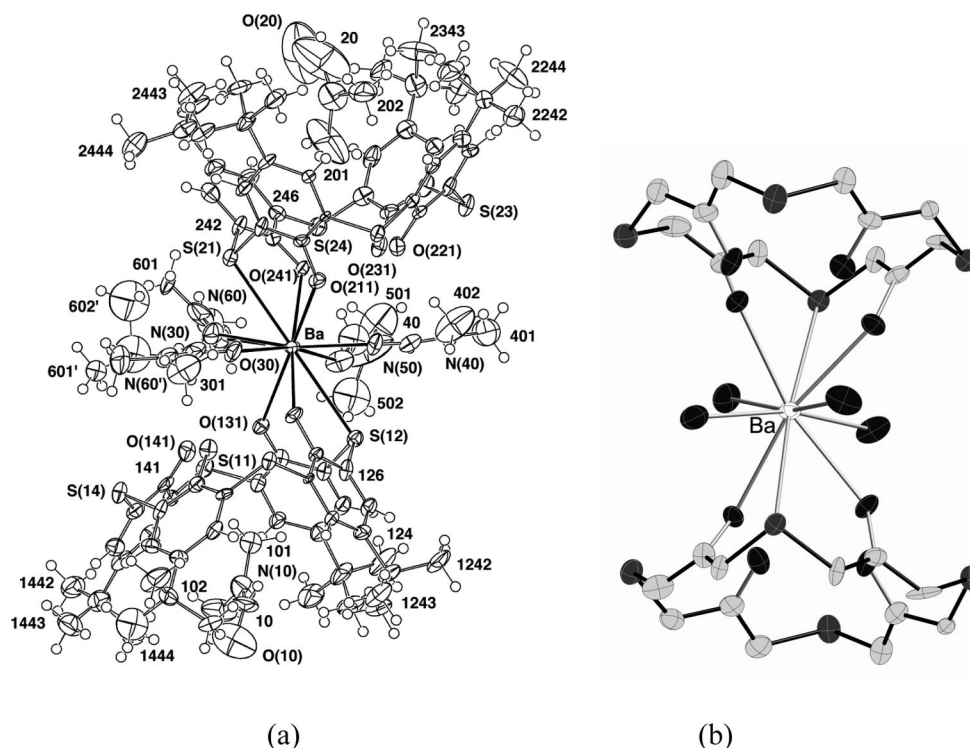
Figure 4. (a) Projection of the molecular array of $[(dmf-O)_4Ba(H_3L \cdot dmf)_2]$ (**2a**) (the quasi-mirror plane approximately in the page). Ba–O(dmf) are 2.750(9)–2.788(9) Å. Within the OSO tripods, Ba–S are 3.404(3), 3.423(3) and Ba–O 2.792(9)–2.820(7) Å. (b) Simplified perspective view of the coordination core of the complex.

columns is 20.625(5) Å. Side by side arrangement of the columns gives rise to sheets parallel to the *ab* plane in which there is a much shorter Ba⋯Ba separation of 11.453(3) Å for neighbouring molecules in adjacent columns, these barium centres forming columns parallel to *a*. "External" CH$_3$⋯π interactions (i.e. from outside the cavity) appear to be involved between such neighbour molecules, whereas between sheets the shortest contacts (ca. 3.8 Å) involve dmf N-CH$_3$ and *tert*-butyl-CH$_3$ carbon atoms. The shortest distance between barium atoms in separate sheets is 19.073(3) Å.

If the calcium-atom environments in the complex **1b** described above were to be described as eight-coordinate CaO$_6$S$_2$ with the sulfur donor atoms adjacent in an irregular array, then in complex **2a** the barium centre is ten-coordinate BaO$_8$S$_2$, with the oxygen atom array almost cubic and the sulfur atoms poised over two opposite cube faces. Both Ba–O and Ba–S bond lengths are approximately 0.4 Å longer than their calcium equivalents. As with the alkali metals,[37,51] both calcium and barium seem to belie their supposedly "hard" nature if there is interaction with sulfur, though the M–S distances are certainly long and, of course, it might be argued that the structure of the calixarene ligand means that binding to oxygen enforces proximity to sulfur. It is plausible also that in systems where the coordinate bonding may be weak no matter what the donor, lattice effects may enforce an unusual situation in the solid. None of the lattice contacts noted above, however, would seem likely to be associated with major interaction energies.[54]

$BaCO_3 \cdot 3Ba(LH_3)_2 \cdot 3H_2O \cdot 3MeCN \cdot 12.25CH_2Cl_2 \equiv$
$[\{(MeCN \cdot LH_3)\text{-}O\text{-}\mu\}_3Ba(\mu\text{-}OH_2)_3(\mu_3\text{-}O,O',O''\text{-}CO_3)Ba_3\text{-}$
$(H_3L \cdot CH_2Cl_2)_3](\cdot 9.25CH_2Cl_2)$ (2b)
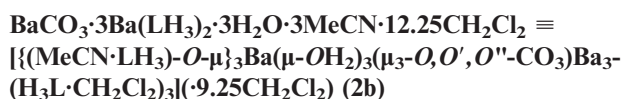
Recrystallisation of complex **2a** from dichloromethane has remarkable consequences and certainly engenders considerable general caution in relating crystal structures to the nature of the species present in bulk solids, especially if they have been precipitated from solvents other than those used for crystal formation. Any mechanism prognosticated for the formation of the present complex can only be considered as pure speculation for the present but the structure is nonetheless a striking example of the novelty that may be found in thiacalixarene coordination chemistry. Its postulation as a solubilised form of BaCO$_3$ suggests the need for sufficiently strong interactions to counteract the lattice energy of that insoluble solid. As with complexes **3, 4b** below, disorder problems, both of the lattice solvent component and the cluster itself (see Experimental), preclude definitive assignment of the hydrogen atom component, particularly in respect of the hydroxylic hydrogen atoms. The formula as given above satisfies charge balance requirements, clearcut insofar as the main group metal is concerned, but other possibilities involving proton transfer between H$_2$O and L groups may be possible, also encompassing hydrogen components which may not necessarily conform to the presumed/assigned crystallographic symmetry. The material crystallises in a lattice of very high symmetry (cubic, $I\bar{4}3d$), as neutral tetranuclear molecular arrays [Figure 5, (a)], the

four barium atoms being disposed quasi-tetrahedrally, with one-third of the array comprising the asymmetric unit of the structure – one apex of the tetrahedron [Ba(2)] lies on a crystallographic 3-axis, with the other three symmetry-related Ba(1) atoms off-axis. The latter are linked by a carbonate group, the plane of which lies normal to the 3-axis with the carbon atom on it, with each oxygen atom approximately equidistant [2.736(9), 2.791(9) Å (Table S4)] from and bridging two Ba(1); the Ba(1) lie out of the CO_3 plane, toward Ba(2), by 0.08(2) Å, each carbonate-*O* acting as a bridge between a pair of barium [Ba(1)] atoms 5.489(2) Å apart rather than each oxygen acting as a unidentate donor

to a single barium atom. With small-ring-chelating ligands such as *O,O'*-carbonate and nitrate, it is of course common to find the OC(N)O chelate unit occupying what may be regarded as a single coordination site.[60] The basal Ba(1)$_3$ triangle is bridged to the apical Ba(2) by three symmetry-related oxygen atoms O(1), presumably derivative of water and assigned as such in the present formulation, although the bridges to Ba(1,2) are unsymmetrical, O(1)···Ba(1,2) being 3.28(1), 2.88(1) Å. The symmetry of the Ba(μ-O)$_3$Ba$_3$ array is degraded from 3*m* to 3 by a twist of the O$_3$ array relative to the basal Ba$_3$ array [Figure 5, (b)]; Ba(1)··· Ba(1′,2) are 5.489(2), 5.448(2) Å.
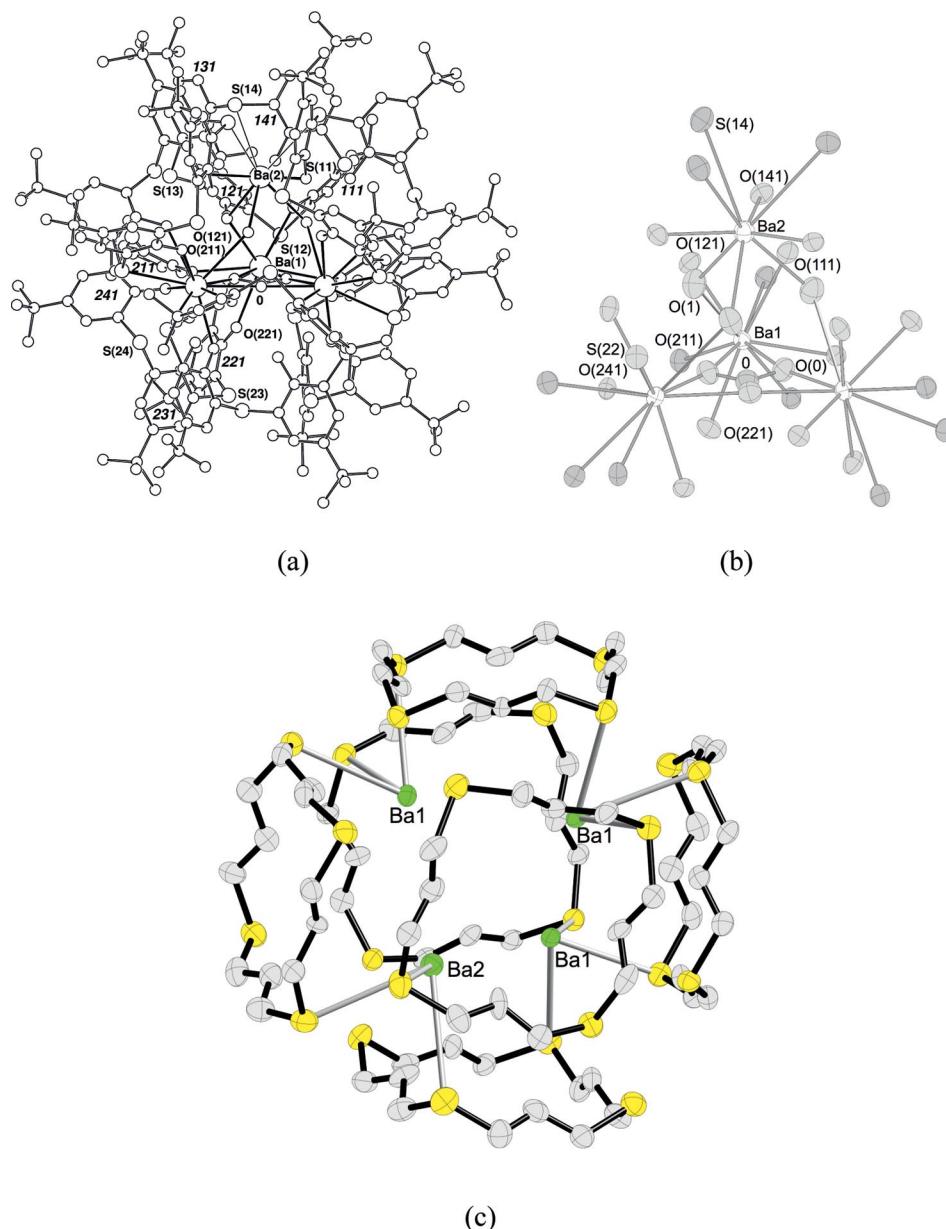

(a)

(b)

(c)

Figure 5. (a) Projection of the tetranuclear array of [{(MeCN·LH$_3$)-*O*-μ}$_3$Ba(μ-OH$_2$)$_3$(μ$_3$-*O,O',O''*-CO$_3$)Ba$_3$(H$_3$L·CH$_2$Cl$_2$)$_3$](·9.25CH$_2$Cl$_2$) (**2b**), approximately normal to the crystallographic 3-axis passing through Ba(2) and C(O$_3$). About Ba(2), Ba(2)–O(1),O(141) are 2.877(11), 2.680(9) Å (both ×3). About Ba(1), Ba-O(carbonate) are 2.736(9), 2.791(9) Å; within the OSO tripods, Ba–S are 3.373(4), 3.293(4) and Ba–O 2.783(9)–2.924(9) Å; Ba(1)–O(241) (*y, z, x*) is 2.777(8) Å. Ligand 1 includes CH$_3$CN, ligand 2 CH$_2$Cl$_2$. (b) The coordination environments in the cluster core. (c) A simplified perspective view of the cluster reduced to the Ba atoms and the C and S atoms of the macrocyclic rings, showing the orthogonally oriented pairs of rings forming an octahedral array.

The whole tetranuclear unit is encapsulated by a quasi-octahedral array of thiacalixarene ligands [Figure 5, (c)]. Each Ba(1) is bound to phenoxy-O(111,121;211,221) from a pair of calixarene ligands, the intervening, more distant sulfur atoms S(12,22) making up somewhat unsymmetrical *fac*-tripods [Table S4, (b)]; ligand 2 links an adjacent basal Ba(1) by a further interaction through O(241). The donor atoms of ligand 2 are generally disposed "below" the basal Ba(1)$_3$ plane, i.e. away from apical Ba(2), while those of ligand 1 lie more generally towards Ba(2). Solvent molecules, modelled as MeCN in ligand 1 and CH$_2$Cl$_2$ in ligand 2, are included in the ligand cavities. O(141) also links the ligand to adjacent Ba, but this time to the apical Ba(2), with the adjacent S(14) also approaching; the dominant components of the Ba(2) environment are thus symmetry-generated triads of aqua [O(1)] and phenoxy [O(141)] oxygen atoms, forming a sparse array in which Ba(2) lies out of the plane of the latter by 0.254(1) Å, so that the only components of the coordination sphere beyond O(141)$_3$ are the distant approaches of S(14)$_3$. Reasons for the remarkable solvent inclusion selectivity shown by the two inequivalent calixarene entities are not obvious. Though there are differences in the calixarene conformations, these are relatively subtle and both may still be described as having close-to-regular *cone* conformations (Table S1).

As is commonly the case when analysing heavy metal compound structures,[61] assignment of the metal ion coordination number can be somewhat arbitrary. If, in the present case, a (generous) limit of 4 Å is set for Ba/donor atom separations to be termed "bonding", all of the barium atoms can be considered twelve-coordinate. However, these interactions include three Ba⋯O contacts at 3.82(1) Å for the apical barium atom and one Ba⋯O at 3.69(1) Å for each basal barium atom. These are all contacts to phenolic oxygen atoms which are within hydrogen-bonding distances of others, so that this may be the factor which is dominant in determining their position in space. In addition, the separations are considerably greater than those for other Ba⋯O contacts [<> 2.8(1) (basal) with one at 3.28(1); 2.8(1) (apical) Å] and even for Ba⋯S [<> 3.38(6) (basal); 3.682(4) (apical) Å]. Hence, it is perhaps best to consider each basal barium atom to be eleven-coordinate or even ten-coordinate if chelating carbonate is taken to occupy a single coordination site, and the apical barium atom to be nine-coordinate. Though bonding to barium is presumably an important determinant of the structure adopted, hydrogen-bonding, as has been noted, is prominent, and, for example, each of the putative water molecules described above as bridging basal and apical barium atoms also lies within strong hydrogen-bonding distance [O⋯O 2.61(1) Å] of a carbonate-*O* atom.

The six thiacalixarene units octahedrally arrayed about each Ba$_4$ unit form a globule with a rather lipophilic exterior, though not one that is uniform, and assembly of the beautifully symmetrical lattice along with a large number of dichloromethane molecules appears to be regulated by a large number of different interactions. Dichloromethane is found not only within the cavities of one set of calixarenes,

but in between adjacent calixarenes of any one tetranuclear aggregate as well as between separate tetranuclear aggregates, seemingly as a result of both CH⋯π and Cl⋯π interactions. Such "solvation" is not, however, so effective as to eliminate some CH$_3$⋯CH$_3$ contacts involving *tert*-butyl groups of separate molecules. The nitrogen atoms of included CH$_3$CN can be regarded as polar points on the globule surface and these atoms have close contacts (ca. 3.5 Å) with non-included Cl atoms from the dichloromethane group. As is true quite generally, while it is relatively easy to discern contacts in a solid-state structure which may be indicative of attractive interactions, it is very difficult to place these interactions in any quantitative order.[62] Viewed as a multiple receptor, this Ba$_4$(thiacalixarene)$_6$ species provides an octahedral array of cavities.

Ga(OH)(LH$_2$)·3.5dmf (×2) ≡ [{(dmf-O)(dmf·LH$_2$)Ga(μ-OH)}$_2$](·3dmf) (3)

In the structures of thiacalixarene complexes of representatives of the group 13 elements, various new features are revealed. Possibly as a reflection of the greater acidity of water bound to a M^{III} species in comparison to M^{II},[63] as well as of the adventitious presence of water in the preparative media, the present Ga^{III} complex has been isolated as a species described in terms of a hydroxo-bridged dimer (Figure 6).
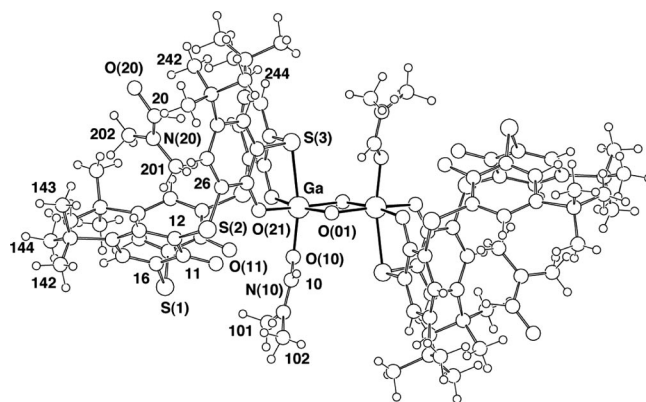

Figure 6. Projection of the binuclear array of 2/*m* symmetry of [{(dmf-O)(dmf·LH$_2$)Ga(μ-OH)}$_2$](·3dmf) (**3**). Ga–O(dmf) is 1.959(8) Å. Within the OSO tripod, Ga–S,O are 2.548(3), 1.941(5) Å (× 2). Within the central Ga$_2$(μ-O)$_2$ rhomb, Ga–O are 1.948(4), Ga⋯Ga 3.023(2), and O⋯O 2.46(1) Å; O–Ga–O and Ga–O–Ga are 78.3(2), 101.8(3)°.

This structure determination (as seems strangely the case with numerous determinations of GaO$_2$Ga arrays), is of inferior precision, perhaps because the protonic hydrogen atoms (which are not defined) may be distributed over a variety of different sites, so that the crystal is a mixture of cocrystallised isomers, perhaps for other reasons. Here, as modelled in space group *Ibam*, the binuclear array lies disposed about a site of 2/*m* symmetry, one quarter of the

dimer comprising the asymmetric unit of the structure. The 2-axis passes through the pair of oxygen atoms, assigned ad hoc as hydroxides, with the mirror plane passing through the gallium atom and the dmf-*O* [the remainder of the dmf being disordered about that plane (as also is the included dmf)], and the sulfur atoms of the thiacalixarene ligand (which is presumed doubly deprotonated), S(3) again forming a *fac*-tripod with the pair of O(21) to either side (Table S5).

The coordination environment about the gallium atom is clearly six-coordinate, quasi-octahedral (Table S5; Figure 6), despite the differences in the M–O,S distances, cf. the previous compounds where the difference was ca. 0.3–0.4 Å but here rises to nearly 0.6 Å, the Ga–O distances being comparable with, e.g., the $[Ga–(OH_2)_6]^{3+}$ distance in (e.g.) $CsGa(SO_4)_2 \cdot 12H_2O^{[64]}$ [1.944(3) Å]. This may be a consequence of different metal–ligand atom binding interactions or of changed constraints arising from the modified ligand conformation about the smaller metal atom, the environment (and ligand disposition) differing markedly from that found in the array of the indium adduct of rather similar stoichiometry, **4a**. Unlike the multinuclear complexes described above and below, the calixarene ligands do not bridge the metal centres [which are only 3.023(2) Å apart], though as in all complexes described so far, the calixarenes, again in close to *cone* conformations (Table S1), are bound through only a limited subset of their eight potential donor centres as OSO tripods. Like **2a**, the Ga^III complex can be considered as a "stepped", divergent ditopic receptor, both cavities of the centrosymmetric species being occupied in the crystal by dmf molecules, the N···N separation [15.21(2) Å] of these included molecules being very similar to that in the barium compound [15.37(2) Å]. Again as in the barium compound, the filled cavities confront one another in such a way that the dimeric complex units form columns parallel to *a*. This confrontation is slightly offset, so that the shortest contacts (ca. 3.3 Å) are found between included dmf-*O* and *tert*-butyl-CH_3 of the adjacent molecule. Links between the dimer columns appear to be largely associated with interactions between the "lattice" dmf and coordinated dmf molecules, though both species are disordered, so that it is difficult to discern differences between possibilities such as dipole alignments or CH···O attractions. The near-octahedral geometry of the primary coordination sphere of the Ga^III is unsurprising,[63,65] and, again, disorder in the bound dmf molecules renders uncertain any evidence that the carbonyl-*C* may be involved in attractive interactions with adjacent nucleophiles (which may include the formally uncoordinated phenolic oxygen atoms). The Ga–O bond lengths, 1.959(8) Å to dmf-*O*, 1.948(4) Å to bridging OH^- and 1.941(5) to calixarene-*O*, all much shorter than Ga–S [2.548(3) Å], fall in a narrow range but are consistent with the proton locations implicit in the assigned formula, albeit not directly located in the structure refinement. The two uncoordinated phenolic oxygen atoms of each calixarene lie within strong hydrogen-bonding distance [2.701(8) Å] of the nearest bound phenolic oxygen atom of the same calixarene entity.

In(LH)·4EtOH·CH_2Cl_2 (×2) ≡ [{(EtOH)In(μ-*O*-{HL·CH_2Cl_2})}_2](·6EtOH) (4a)
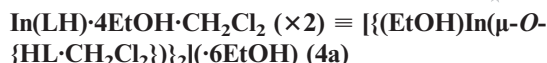
As was the case with group 2, crystallisation of the heavier group 13 metal (In) complex from different solvents provided different species, though here the changes were somewhat less radical than those observed for Ba^II. From dichloromethane/ethanol, In^III provided (from a seemingly amorphous dmf solvate) the present dimeric complex. This structure is precise and devoid of disorder; the dimer is disposed about a crystallographic inversion centre, so that one-half comprises the asymmetric unit of the structure. In consequence of crystallisation from a mixed solvent system, an interesting and well-defined solvation pattern, perhaps a critical prerequisite of crystallisation, is found, the cavity of the ligand including CH_2Cl_2 (Figure 7), while voids in the lattice are occupied by ethanol. Although some water may also be presumed to be present in the solvent, the pair of metal atoms, rather than being bridged by a(n) (hydr)oxo species, are linked by a pair of thiacalixarene ligands, being bridged by one of the deprotonated ligand phenoxo-*O* atoms of each. Two others in each ligand are also deprotonated and bond symmetrically to either side to the indium atoms. Together with the intervening sulfur atoms, again at relatively long distances, they provide (double) facial tripodal components [2 × OS(O-μ); common O-μ] of the coordination sphere of the indium, which here has a seven-coordinate (O_5S_2) stereochemistry (Tables S1, S6), approximately pentagonal bipyramidal, the two sulfur atoms in the plane. The tripodal In–O distances are unsymmetrical, the shorter corresponding to the deprotonated bridging oxygen atoms. Compared to Ga–O, the In–O distances fall in a wide range [2.071(3)–2.523(4) Å], with In–O(dmf) longest [Figure 7, (a)], so that the distinction from In–S [2.663(1), 2.650(1) Å] is not so clearcut. The uncoordinated phenolic OH group (31) interacts with the adjacent deprotonated phenoxo-*O* atoms O(41) via the shortest of the ligand O···O distances (Tables S1, S6). The dihedral angle between the central In_2O_2 plane and the ligand O_4 plane is 60.7(1)°.

The In–H*O*Et distance is long; the ethanol hydroxy groups hydrogen-bond among themselves [O,H(101)···O(301) (*x*, *y*, 1 + *z*) 2.750(5), 1.9_3; O,H(201)···O(401) 2.750(7), 1.7_6; O,H(301)···O(201) (*x*, *y*, *z* – 1) 2.716(7), 1.7_6] except for O,H(401) which interacts with O(21) of the ligand [2.906(5), 2.2_2 Å]. The aromatic C_6 planes of the ligand in this complex lie more nearly aligned with the cone axis, the O···O distances all exceeding 2.76 Å (Table S1).

The structure of **4a** is unlike that of **3** in that dimerisation can be seen as concomitant of bridging by the calixarene ligands and not by exogenous hydroxide (perhaps a reflection of weaker acidity for In^III–OH_2 cf. Ga^III–OH_2, as certainly some water would have been available in the undried ethanol). As in the dimeric Ca^II complex, the calixarene ligands are of denticity five (cf. three in **2a**) but here there is an appreciable stretching of the *cone* conformation towards *2m* symmetry, seen also in the alignment of the Cl–C–Cl plane of included dichloromethane with the longer axis of its rectangular profile. The residual phenolic proton
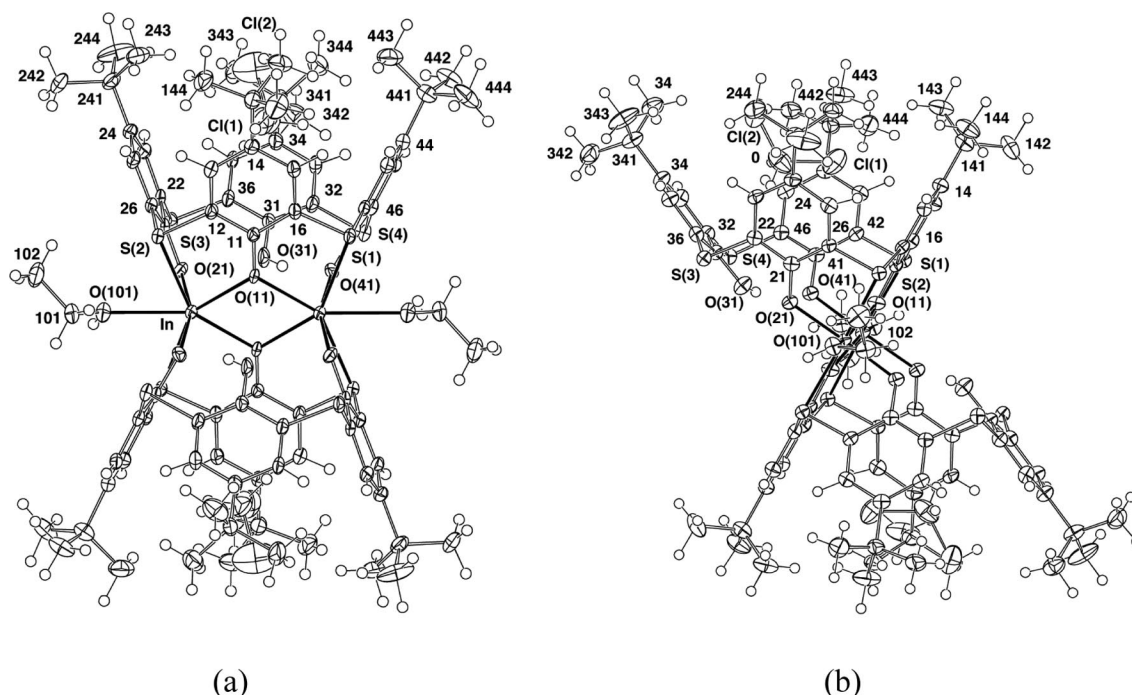
(a)   (b)

Figure 7. Projections of the centrosymmetric binuclear array of [{(EtOH)In(μ-*O*-{HL·CH$_2$Cl$_2$})}$_2$](·6EtOH) (**4a**): (a) through the In$_2$O$_2$ core [In–O(dmf) is 2.522(4) Å. Within the OS(O-μ) tripods In–O(μ) are 2.237(3), 2.237(4), In–O(outer) (deprotonated) 2.071(3), 2.088(3), In–S 2.663(1), 2.650(1) Å. Within the central In$_2$(μ-O)$_2$ rhomb, In···In is 3.6728(9), O···O 2.555(4) Å; O–In–O and In–O–In are 69.6(1), 110.4(1)°]; (b) along the In···In axis.

could be refined as present on the uncoordinated phenolic unit and is within hydrogen-bonding distance of the bridging phenoxide-*O* of the same calixarene, a situation true for both macrocyclic ligands since the complex is centrosymmetric.

The complex can again be termed a "stepped", divergent ditopic receptor and, once more, these receptors, with their dichloromethane guests, form columns in the lattice in which the calixarene cavities are in slightly offset confrontation. The dichloromethane molecules appear to be held within the cavities by both CH···π and Cl···π interactions but they are also involved in the shortest contacts (Cl···CH$_3$ ca. 3.7 Å) across the "gap" between facing cavities within the columns. Ethanol is excluded from the cavities, presumably because of stronger interactions, relative to those of dichloromethane, involving coordination to In^{III} and hydrogen-bonding to both itself and phenolic groups, and a different symmetry.

In(OH)(LH$_2$)·3CH$_2$Cl$_2$ (×4) ≡ [{In(μ-*OH*)(μ-*O*-{H$_2$L·CH$_2$Cl$_2$})}$_4$](·8CH$_2$Cl$_2$) (4b)
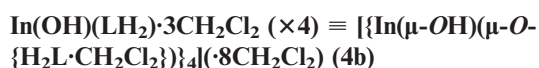
Many of the considerations involved in most of the previous arrays become relevant in considering the nature of compound **4b**, which is most simply considered as a hydrolysis product of **4a**, the change of solvent to dichloromethane alone seemingly being sufficient to cause a reaction which does not occur in ethanol. Here, despite good quality data, and an oligonuclear aggregate in which displacement amplitudes are mostly congenial, proper definition of the

nature of the structure is critically dependent on hydrogen atom definition and location, which is thwarted by widespread disorder among the non-included lattice dichloromethane molecules of solvation, and, also, one of the *tert*-butyl substituents of the ligand. In consequence, although the overall protonic hydrogen count may be presumed well-defined consequent on the well-defined valence state of the main group metal, the distribution of such hydrogen components between bridging oxygen atoms and phenoxy-*O* atoms remains an open question. Moreover, although the complex is tetranuclear, disposed about a $\bar{4}$ crystallographic axis in space group $I\bar{4}$, there is no necessity that protonic hydrogen atoms are disposed symmetrically about the In$_4$O$_4$ core or about the ligands. However, with this assumption, the compound may be formulated as given above, with various combinations of deprotonation of ligand and aqua bridges being possible, so that formulations such as [In$_4$({LH·CH$_2$Cl$_2$})$_4$(OH$_2$)$_4$]·8CH$_2$Cl$_2$ are also plausible. Given that the In–OH$_n$ distance [2.061(8) Å] is the shortest of all In–O distances found in either of the present complexes, the "hydroxy" formulation is perhaps preferable. [However, we note that the Cambridge Crystallographic Data Base[66] currently contains no definitive examples of pairs of indium atoms bridged by H$_2$O, while those which are O-bridged have In–O–In "normally" greater than 135°, cf. the present 117.6(3)°]. One quarter of the tetranuclear substrate comprises the asymmetric unit of the structure. The four indium atoms are linked into a square by pairs of oxygen bridges, one of each pair derivative of water appropriately deprotonated, the other from a(n almost certainly

deprotonated) bridging phenoxide oxygen, each ligand linking pairs of indium atoms in much the same way as in **4a**, i.e. the pair of phenoxy-*O* atoms to either side, bound at similar distances, and the two intervening sulfur atoms coordinating the two indium atoms facially, i.e. the ligand again provides a 2 × OS(*O*-μ), common *O*-μ tripod set (Figure 8).
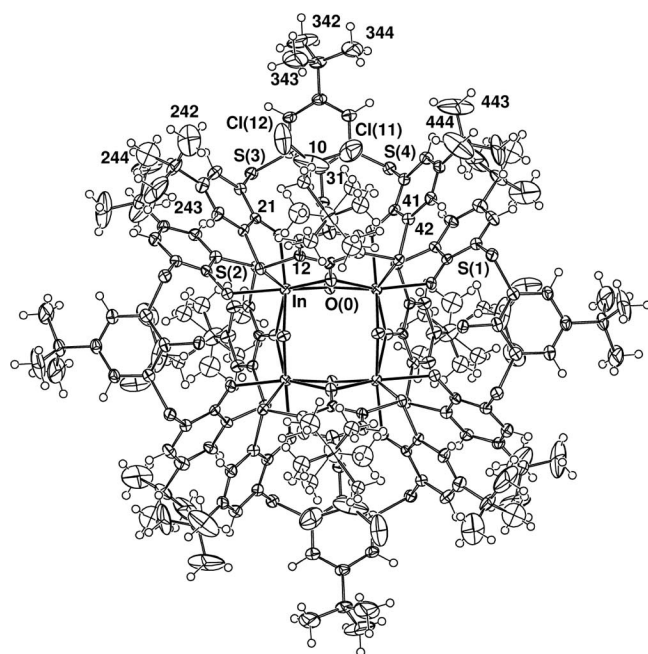
(a)
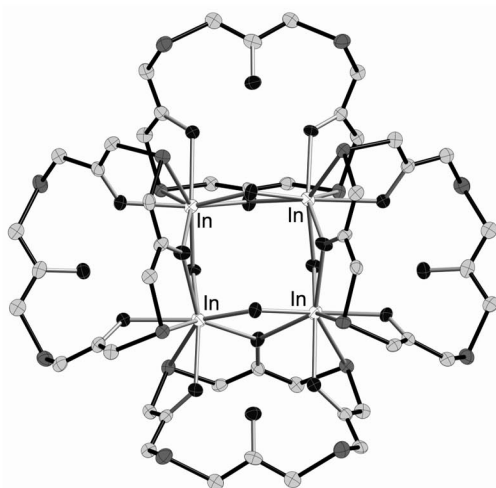
(b)

Figure 8. (a) Projection of the tetranuclear array of [{In(μ-*O*H)(μ-*O*-{H$_2$L·CH$_2$Cl$_2$})}$_4$]·(8CH$_2$Cl$_2$) (**4b**) down its $\bar{4}$ axis. In–O(H) are 2.061(2), 2.159(8) Å. Within the OS(*O*-μ) tripods, In–S are 2.838(3), 2.910(3), In–O(μ) 2.336(8), 2.346(8) and In–O(outer) 2.201(6), 2.330(6) Å. Within the In$_2$O(H)(μ-O) rhombs, In···In is 3.6107(8) and O···O 2.55(1) Å; O–In–O, In–O–In are 70.5(3), 117.6(3)°. (b) A simplified, perspective view of the coordination core showing the tetrahedral array of the macrocyclic rings.

ure 8). The indium atoms may be considered eight- rather than seven-coordinate (as in **4a**) with In–O,S correspondingly longer [Table S6, (b)].

The tetranuclear entity of **4b**, having $\bar{4}$ symmetry, can be considered a divergent, flattened tetrahedral receptor, each cavity being occupied by dichloromethane in the present crystal; the tetrameric aggregate itself has also a large pore through its centre, along the $\bar{4}$ axis which also hosts approaching disordered dichloromethane. The calixarene denticity (five) is the same as in the dimer complex, and distortion of the calixarene conformation from a true *cone* is similar (Table S1), with the two phenyl rings on the axis parallel to a line joining the In···In pair [3.6107(8) Å apart] bridged by the calixarene being less tilted with respect to the mean S$_4$ plane than the other two. Each indium atom has O$_6$S$_2$ eight-coordination of approximately dicapped trigonal prismatic geometry, with In–S being ca. 0.5 Å longer than even the longest In–O. Although many open, diamondoid structures are known to be generated from molecules which may be considered large, tetrahedral connectors,[67] in the present case the tetranuclear units do not aggregate by face-to-face confrontation of their calixarene cavities. Contacts instead involve external CH$_3$···π approaches along with numerous interactions involving the large number of dichloromethane molecules, included and not, so that the lattice is quite compact.

OPb$_4$(LH)$_2$·6dmf·dmso·2H$_2$O ≡ [(μ$_4$-O){Pb(*O*-dmf/dmso)}$_2${Pb(*O*-dmf)(*O*H$_2$)}$_2$(LH·dmf)$_2$](·dmf) (5)
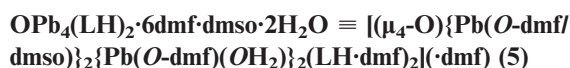
To find a complex of *p-tert*-butyltetrathiacalix[4]arene with a main-group metal in which all *O*- and *S*-donor centres are involved in coordination, it is necessary to pass to Pb^{II}. This complex has a complicated stoichiometry, formulated as **5** on the basis of its structure determination, reflecting the use of a reactant dmso complex in incompletely dry dmf solvent, but the structure (Figure 9), of an elegant form, is closely related to that known for the Nd^{III} complex.[42] Protonic hydrogen atoms, if present, are undefined by the present X-ray experiment. However, the gross stoichiometry may be assigned with reasonable confidence in view of the nature of the oxo-species, the long O···O distances in the ligand and the probable oxidation state of the lead as lead(II), so that a neutral molecular aggregate is presumed (but see below).

Again the array is tetranuclear, but with a different relationship between the Pb$_4$ array and the associated macrocycle ligands, increasing the diversity further. The aggregate is disposed about a crystallographic inversion centre, one half comprising the asymmetric unit of the structure; the four lead atoms are necessarily coplanar and coplanar with the residue assigned as the oxo-group, located on the inversion centre. It involves a true "sandwich" in which a Pb$_4$O entity is held between a pair of opposed calixarene *cone* units, so that as a molecular tecton it may be regarded as a simple linear connector. In the present complex, each cavity is occupied by a dmf molecule (methyl group included) and

the sheets of complex entities which form parallel to the *ac* diagonal and perpendicular to the *ac* plane are arranged relative to one another such that the cavities are in dis- placed confrontation enabling close included-dmf-*O*/CH$_3$ contacts (as short as 3.5 Å) across the interface. The pres- ence of four diverse unidentate ligands coordinated in the
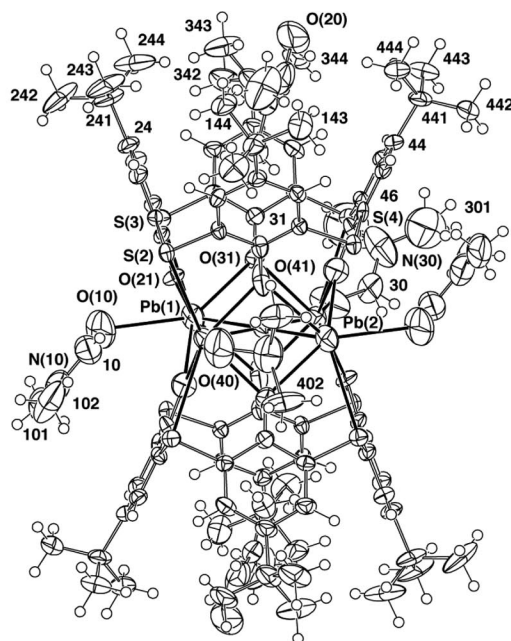
(a)
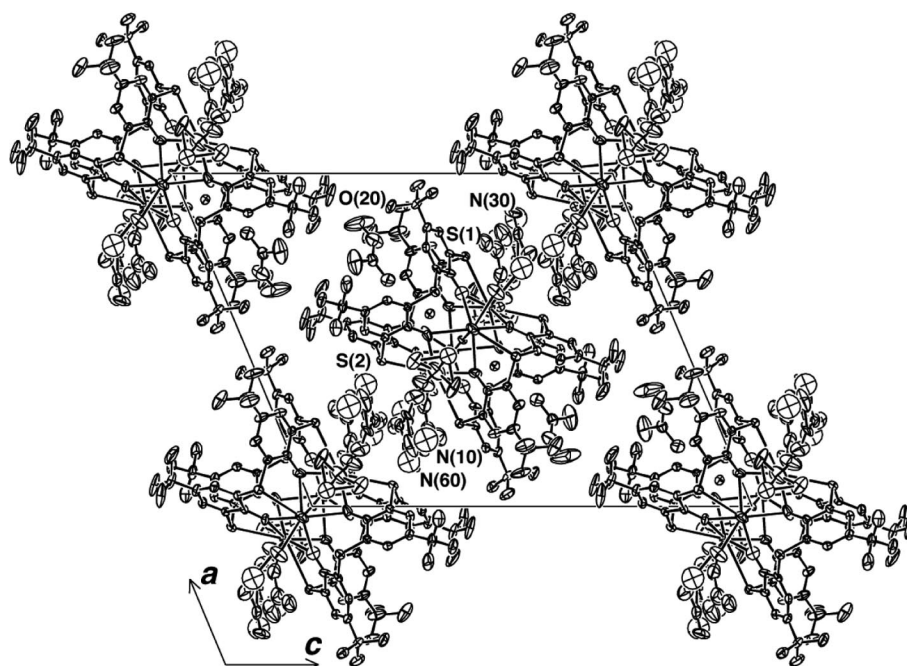
(b)

Figure 9. (a) Projection of the tetranuclear array of [(μ$_4$-*O*){Pb(*O*-dmf/dmso)}$_2${Pb(*O*-dmf)(OH$_2$)}$_2$(LH·dmf)$_2$](·dmf) (**5**) (major compo- nent) normal to its quasi-4 axis. For the major (unprimed) component, O(central)–Pb(1,2) are 2.4829(3), 2.7055(4) Å. Pb(1)–O(dmso) is 2.765(9); Pb(2)–O[dmso/dmf, O(H$_2$)] 3.04(1)/2.75(2), 3.70(2) Å. Within the S(μ-O) tripods, Pb–S are 3.111(2), 3.161(2) and Pb–O 2.506(7)– 2.583(7) Å. (b) Unit cell contents, projected down *b*.

Pb$_4$O plane – one dmso [disordered over two inversion-related sites and coordinated to Pb(2)] and three dmf (one disordered in concert with the dmso in the centrosymmetric model) – is associated with the lead atoms being inequivalent, with significantly different bond lengths to the central oxygen atom [Pb(1,2)–O(0) 2.7055(4); 2.4829(3) Å], though both may be regarded as approximately dicapped trigonal prismatic PbO$_6$S$_2$ centres, with <Pb–S> ca. 0.5 Å longer than <Pb–O> (though with a wide range in the latter). There are large voids in the coordination spheres of the lead atoms, opposite the central-O–Pb bonds (Table S7, Supporting Information), the associated S–Pb–S angles being 132.79(5), 125.90(4)°, with long distances to the oxygen atoms of the lattice dmf molecules, perhaps indicative of sterically active lone pairs. The Pb···Pb distances on the edges of the square are essentially identical, 3.6688(4), 3.6754(5) Å, separations close to the minima found in the PbO forms litharge and massicot,[68] but the Pb···Pb···Pb angles deviate appreciably from 90°, that at Pb(1) being 85.09(1) and at Pb(2) 94.91(1)°, although the angles about O(0) are close to orthogonality. The two macrocycles approach from either side of the OPb$_4$ plane, superimposing on each other in projection down the calix axis, and in such a manner that each oxygen donor nearly symmetrically bridges pairs of lead atoms, with the sulfur atoms also pairwise above and below each lead, so that, peripheral pendants aside, the OPb$_4$(macrocycle)$_2$ array has quasi-*4/mmm* symmetry, reduced to *4/m* by the in-plane solvent ligands. Returning to the curious asymmetry in the central-O–Pb distances, and the question of the protonation of the aggregate, we note that O(0)···O(n1) are (*n* = 1–4) 2.794(7), 2.992(5), 2.845(6), 2.844(7) Å, distances shorter than those between O(n1)···O(n1′) of the calix, raising the possibility of hydrogen-bonding (disordered) between the central oxygen atom and the phenolic oxygen atoms as definitive (in general terms) of the protonic hydrogen dispositions; there are also differences in the pairs of Pb–O distances within each (μ-O)$_2$S *fac*-tripod. Also curious is the assembly of residues modelled as minor components of lead atoms (see Experimental), one lying above the central oxygen atom [Pb(1′)] and the other, Pb(2′), 0.599(4) Å from Pb(2), refining in concert to an occupancy of 0.0745(6). Pb(1′,2′) lie 2.332(4), 2.906(3) Å from the central oxygen atom, comprising, with their inversion images, a secondary Pb′$_4$O array, with Pb(1′)···Pb(2′) (and its inversion image) 4.007(3), 3.423(5) Å, and with a dihedral angle of 88.23(7)° to the primary Pb$_4$O plane. Insofar as those relate to the present ligand arrays, presumably to be regarded also as major components, but probably at least as far as the calixarenes are concerned, in similar dispositions, the environs of Pb(1′), made up of one thiacalixarene ligand as a tolerably symmetrical tetradentate donor, together with the central oxygen atom, are credible, albeit sparse, with a large void opposite the central oxygen atom; Pb(1′) lies out of the phenoxy-O$_4$ plane by 0.644(4) Å, into the calix where it lies 3.01(1) Å from one of the methyl groups of the included dmf. There is, however, no certainty that this represents the orientation of any included unresolved minor component

and it may be that any such interaction is different in nature. Pb(2′) interacts with an oxygen pair from each of the two thiacalixarenes; interaction with dmf O(30) in its present location is also credible, that with O(40) not, although O(70), assigned as a putative water molecule oxygen atom, now comes into consideration. A possible explanation is that the primed array thus represents the basis of a different isomer or complex, cocrystallised, or some similar form of disorder.

Conclusions

To establish what we consider to be basic coordination chemistry of *p-tert*-butyltetrathiacalix[4]arene, we have limited our investigations to systems where donor atoms other than those of the calixarene are derived only from solvent molecules or simple anions. In total, this has allowed us to establish a considerable body of structural information, the significance of which we analyse further in the final part of this work,[53] in order to take as broad a context as possible. Thus, as intermediate conclusions, we note that the present report establishes four structures for group 2 metal ion [Ca(× 2),Ba(× 2)] complexes, three for group 13 metal ions [Ga, In(× 2)] and one for a group 14 metal ion (Pb^{II}). The calixarene is found exclusively in its *cone* conformation despite differences in the bound metal and the degree of deprotonation. While several of these structures define approximate "sandwich" forms, varying in their closure, as seen with various other metal ions,[18–46] the structures of the tetranuclear Ba and In complexes define forms that have not been previously observed. Although significant differences in the bonding preferences of the various metal ions might have been anticipated, in all cases the thiacalixarene behaves as an O- and S-donor even when, ignoring proton coordination, the ligand denticity varies between 3 (for Ca, for example) and 8 (for Pb^{II}). Differences between the metal ions are presumably the cause of the different degrees of deprotonation of the thiacalixarene observed as well as of the presence of oxo- and hydroxo- ligands, the Pb^{II} complex, with a planar Pb$_4$O rhomb sandwiched between two maximally coordinating, fully deprotonated (μ-O)$_4$(μ-S)$_4$ calixarene units, having a structure remarkably like that of the Nd^{III} complex.[42] It is clear that the bound calixarene, at least when an approximate *cone* form is retained, can act as a receptor for neutral molecules, though the origins of the apparent selectivity of inclusion presently observed in some cases is unclear. A question that remains is whether the "cluster keeping" and inclusion properties of thiacalixarene complexes can be utilised together in the construction of specific arrays of multimetal units.

Experimental Section

Synthesis and Crystallisation: Because the principal objective in the present work was to obtain crystalline materials suitable for X-ray structural characterisations as definitively as possible, and not necessarily to optimise isolated yields, no doubt most of the syn-

thetic procedures could be improved in regard to the latter factor. In both the present and associated work,[52,53] it was commonly found, as for published cases,[30,36–39,42–44] that the complexes could be formed readily by reaction of a solvated metal salt such as $[M(dmso)_n](ClO_4)_x$ in a dipolar, aprotic solvent (such as dimethyl sulfoxide, dmso) with a solution of the thiacalix[4]arene [LH_4, prepared as in the literature[18] as its chloroform solvate, ($LH_4 \cdot CHCl_3$)] and triethylamine in the same solvent (though other methods are known[28]). Sometimes, this led only to the crystallisation of the triethylammonium derivative of the calixarene monoanion.[37a] More frequently, the initial products were extremely insoluble in the preparative solvent (thus essentially impossible to recrystallise under the same conditions as for their synthesis) and recrystallisation could only be achieved through the use of mixtures of other solvents, resulting, in a number of instances, in remarkably complicated compositions with respect to the variety of solvents shown to be present by the structure solutions for the final crystals. Crystallisations were usually conducted in loosely sealed systems, using various procedures including both liquid and vapour diffusion, but without stringent precautions to avoid contact with a humid normal atmosphere, presumably the reason for the observed presence of water and its conjugate bases in many of the recrystallised materials. For these and other reasons (see Discussion), it must be stated that the present investigations of the syntheses can only be regarded as preliminary and that many of the structurally characterised species are probably not the initial products of the reactions conducted. The formulae given to identify each compound are those modelled by the structure solutions. For group 2 in particular, considerable effort was expended in attempting to provide characterisation as complete as that presented previously for the group 1 complexes but crystals appropriate for structure determinations were obtained with Ca and Ba only.

Mg: A ground mixture of $Mg(CH_3CO_2)_2 \cdot 4H_2O$ (42 mg) and *p-tert*-butyltetrathiacalix[4]arene chloroform solvate [($LH_4 \cdot CHCl_3$), 84 mg] was stirred with hot (130 °C) dmso (2 mL) for 5 min. The clear solution formed was filtered, cooled to room temperature and allowed to stand thus for several days as clusters of rod-like crystals (which diffracted very poorly) slowly deposited.

Ca(LH$_3$)$_2$·3dmf (1a): A solution of $[Ca(dmso)_6](ClO_4)_2$[59] (130 mg) in dmf (1 mL) was mixed with a solution formed by adding ($LH_4 \cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.1 mL) to dmf (1 mL). The initially clear solution was allowed stand for 2 d as colourless plate-like crystals deposited. A crystal suitable for a structure determination was selected before the bulk precipitate was collected, washed on the filter with a little ether and dried under vacuum. Yield: 93 mg. Microanalysis of this material (exposed to the atmosphere after initial drying) was consistent with a higher degree of solvation than indicated by the structure solution: $Ca(LH_3)_2 \cdot 5dmf \cdot 3H_2O = C_{95}H_{135}N_5CaO_{16}S_8$ (1899.7): calcd. C 60.07, H 7.16, N 3.69, S 13.50; found C 59.7, H, 6.5, N, 3.4, S 14.0%.

Ca(LH$_2$)·3dmf (×2) (1b): The preceding synthesis was repeated but with the use of 170 mg of $[Ca(dmso)_6](ClO_4)_2$ (the correct quantity for a 2:1 ratio of Ca/calixarene). Again, colourless crystals, assumed, until the structure solution was obtained, to be the same material, were deposited in similar yield (95 mg). Analysis was consistent with some degree of hydration of the stored, bulk material: $Ca(LH_2) \cdot 3dmf \cdot 2H_2O (\times 2) = C_{98}H_{142}Ca_2N_6O_{18}S_8$ (2028.9): calcd. C 58.53, H 7.12, N 4.18, S 12.76; found C 58.2, H 7.1, N 4.6, S 11.8.

Sr: Repetition of both the above syntheses using $Sr(ClO_4)_2 \cdot 6dmso$[59] (75 mg) in place of the $[Ca(dmso)_6](ClO_4)_2$ provided no crystalline nor even just insoluble material. Changing the solvent

to dmso gave the same result. As an alternative, solid $Sr(ClO_4)_2 \cdot 6dmso$ (90 mg, 20% excess above a 1:1 ratio) was added to a solution of ($LH_4 \cdot CHCl_3$) (84 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in CH_2Cl_2 (2 mL). Vigorous mixing for 30 s produced a seemingly homogeneous solution, which was concentrated to dryness and the residue extracted with CH_2Cl_2 (4 mL). The very small amount of flocculent colourless material which remained insoluble was filtered out and the filtrate diluted with ethanol (2 mL). This final clear solution was allowed stand in an open vial for the CH_2Cl_2 to evaporate out and colourless tablets, again of inappropriate quality to permit a diffraction study, began to crystallise after 1 h.

Ba(LH$_3$)$_2$·6dmf (2a): Solutions of $Ba(ClO_4)_2 \cdot 3H_2O$ (460 mg) in dmf (3 mL) and ($LH_4 \cdot CHCl_3$) (500 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmf (5 mL) were mixed, filtered and the filtrate allowed to stand at room temperature in a stoppered vial as lustrous, colourless crystals very slowly deposited. After one month, a crystal was selected for a structure determination and the bulk was then collected, washed with CH_3CN and dried in vacuo. Yield: 422 mg. Again, microanalysis indicated that isolation, drying and brief storage of the material resulted in some change in solvation compared to the single crystal: $Ba(LH_3)_2 \cdot 4dmf \cdot 6H_2O = C_{92}H_{134}BaN_4O_{18}S_8$ (1978.0): calcd. C 55.86, H 6.83, N 2.83; found C 55.7, H 6.2, N 2.9.

BaCO$_3$·3Ba(LH$_3$)$_2$·3H$_2$O·3MeCN·12.25CH$_2$Cl$_2$ (2b): CH_3CN (5 mL) was layered onto a solution of crude $Ba(LH_3)_2$ 6dmf (20 mg) in CH_2Cl_2 (5 mL) and the mixture left in a stoppered tube for 1 month. The crystalline deposit formed consisted of a mixture of plates and clusters of rods, one of the plates being used for the structure determination.

Ga(OH)(LH$_2$)·3.5dmf (×2) (3): $[Ga(dmso)_6](ClO_4)_3$[64] (400 mg) in dmf (4 mL) was added to a solution of ($LH_4 \cdot CHCl_3$) (200 mg) and $N(CH_2CH_3)_3$ (0.2 mL) in dmf (10 mL). The resulting colourless solution was left to stand at room temperature in a stoppered flask for 10 d as thin colourless needles slowly deposited. A crystal was selected for a structure determination before the bulk was collected, washed with diethyl ether and allowed dry in air. Yield: 82 mg. Analysis was consistent with some hydration of the isolated material: $Ga(OH)(LH_2) \cdot 3.5dmf \cdot 1.5H_2O (\times 2) = C_{101}H_{149}Ga_2N_7O_{20}S_8$ (2177.3): calcd. C 55.72, H 6.90, N 4.50, S 11.78; found C 55.8, H 6.9, N 4.5, S 11.8.

In(LH)·4EtOH·CH$_2$Cl$_2$ (×2) (4a): $[In(dmso)_6](ClO_4)_3$[69] (520 mg) in dmf (2 mL) was added to a solution of ($LH_4 \cdot CHCl_3$) (250 mg) and $N(CH_2CH_3)_3$ (0.25 mL) in dmf (5 mL). The resulting yellow solution was filtered and the filtrate allowed to stand open to the atmosphere for 1 week as an amorphous white solid deposited. This was collected, washed with dmf and dried in air. Yield: 270 mg. To obtain crystals suitable for a structure determination, the crude material (15 mg) was dissolved in CH_2Cl_2 (1.5 mL) and ethanol (0.5 mL) layered on top of this solution. Quantitative precipitation of colourless tablets occurred over several days.

In(OH)(LH$_2$)·3CH$_2$Cl$_2$ (×4) (4b): If the crude material obtained above were simply dissolved in CH_2Cl_2 and the solution concentrated by slow evaporation of the solvent, crystals of this tetrameric species were obtained. Both the tetramer and dimer complex crystals were efflorescent and microanalyses close to those required for the formulations deduced from the structure solutions (and given here) could not be obtained, though C, H figures on the dried tetramer were close to those for a species $In(OH)(LH_2) \cdot 0.5CH_2Cl_2$ (× 4) = $C_{162}H_{188}Cl_4In_4O_{20}S_{16}$ (3573.5), having lost lattice solvent only: calcd. C 54.45, H 5.42; found C 54.5, H, 5.5%.

OPb$_4$(LH)$_2$·6dmf·dmso·2H$_2$O (5): $[Pb(dmso)_5(O_2ClO_2)]ClO_4$[70] (210 mg) in dmf (4 mL) was added to a solution of ($LH_4 \cdot CHCl_3$)

(100 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmf (10 mL), the clear initial solution quickly filtered and the filtrate allowed stand for 5 min as colourless prismatic crystals deposited. After selection of a crystal for a structure determination, the bulk was collected, washed with hexane and air-dried. Yield: 119 mg. Analysis corresponded to the loss of one molecule of dmf from the crystalline material: $OPb_4(LH)_2 \cdot 5dmf \cdot dmso \cdot 2H_2O = C_{97}H_{135}N_5O_{17}Pb_4S_9$ (2760.6): calcd. C 41.81, H 4.67, N 1.61, S 11.04; found C 41.7, H 4.5, N 1.7, S 10.5.

Structure Determinations: (Generally applicable to the present and associated[52,53] pair of papers). Full spheres of low-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans, monochromatic Mo-K_α radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique after empirical/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed" and used in the large block/full-matrix least-squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$ being included, with idealised geometries where possible. Conventional residuals R, R_w on $|F|$ at convergence are cited {reflection weights: $[\sigma^2(F) + 0.0004\ F^2]^{-1}$}. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[71] Pertinent results are given below and in the Tables and Figures the latter showing 50% probability displacement amplitude envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å, and carbon atoms being denoted by number only; where metal atom environments are presented in matrix format, r [Å] is the metal-donor atom distance, the other entries being the angles (degrees) subtended at the metal by the relevant atoms at the head of the row and column. Individual divergences/variations in procedure are cited as "*variata*". Ligand (calixarene) geometry is detailed in a comparative manner for all complexes in Tables S1 and S2, in particular. CCDC-623511 (**1a**), -623512 (**1b**), -623513 (**2a**), -623514 (**2b**), -623515 (**3**), -623516 (**4a**), -623517 (**4b**) and -623518 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal/Refinement Data

Ca(LH₃)₂·3dmf ≡ [(dmf-*O*)₂Ca(H₃L)(H₃L·dmf)] (1a)

$C_{89}H_{115}CaN_3O_{11}S_8$, $M = 1699.5$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 11.472(1)$, $b = 17.072(7)$, $c = 24.458(2)$ Å, $\alpha = 72.245(1)$, $\beta = 83.987(2)$, $\gamma = 84.125(2)°$, $V = 4524$ Å³. D_c ($Z = 2$) = 1.24_8 g cm⁻³. $\mu_{Mo} = 3.1$ cm⁻¹; specimen: $0.45 \times 0.38 \times 0.20$ mm; $T_{min./max.} = 0.84$. $2\theta_{max.} = 58°$; $N_t = 49360$, $N = 22009$ ($R_{int} = 0.032$), $N_o = 16084$; $R = 0.056$, $R_w = 0.065$.

Variata: $(x,y,z,U_{iso})_H$ were refined for the hydroxy hydrogen atoms, O(121,211) being deprotonated. The pendant atoms of coordinated dmf 3 are disordered over two orientations, site occupancies set at 0.5 after trial refinement.

Ca(LH₂)·3dmf (×2) ≡ [{(dmf-*O*)₂Ca}₂{μ-*O*,*O*′,*O*″-(H₂L·dmf)}₂] (1b)

$C_{98}H_{134}Ca_2N_6O_{14}S_8$, $M = 1956.9$. Monoclinic, space group $P2_1$ (C_2^2, No. 4), $a = 12.722(2)$, $b = 22.117(3)$, $c = 18.433(2)$ Å, $\beta = 94.801(2)°$, $V = 5168$ Å³. D_c ($Z = 2$) = 1.25_7 g cm⁻³. $\mu_{Mo} = 3.3$ cm⁻¹; specimen: $0.15 \times 0.12 \times 0.09$ mm; $T_{min./max.} = 0.78$. $2\theta_{max.} = 58°$; $N_t = 52120$, $N = 13020$ ($R_{int} = 0.090$), $N_o = 6977$; $R = 0.065$, $R_w = 0.061$. $x_{abs.} = 0.22(7)$.

Variata: *tert*-Butyl group 234 was modelled as rotationally disordered about the pendant bond, site occupancies of the two loca-

tions refining to 0.77(3) and complement. Phenolic hydrogen atoms were not located.

Ba(LH₃)₂·6dmf ≡ [(dmf-*O*)₄Ba(H₃L·dmf)₂] (2a)

$C_{98}H_{136}BaN_6O_{14}S_8$, $M = 2010.1$. Triclinic, space group $P\bar{1}$, $a = 11.453(3)$, $b = 20.625(5)$, $c = 24.139(6)$ Å, $\alpha = 72.462(4)$, $\beta = 89.869(2)$, $\gamma = 89.779(4)°$, $V = 5437$ Å³. D_c ($Z = 2$) = 1.23_1 g cm⁻³. $\mu_{Mo} = 5.8$ cm⁻¹; specimen: $0.35 \times 0.35 \times 0.06$ mm; $T_{min./max.} = 0.79$. $2\theta_{max.} = 50°$; $N_t = 63565$, $N = 19057$ ($R_{int} = 0.069$), $N_o = 15375$; $R = 0.12$, $R_w = 0.15$.

Variata: One of the coordinated dmf ligands (#6) was modelled as disordered about the pendant bond over two sets of sites, occupancies set at 0.5 after trial refinement. Phenolic hydrogen atoms were not located.

BaCO₃·3Ba(LH₃)₂·3H₂O·3MeCN·12.25CH₂Cl₂ ≡ [{(MeCN·LH₃)-*O*-μ}₃Ba(μ-*OH*₂)₃(μ₃-*O*,*O*′,*O*″-CO₃)Ba₃(H₃L·CH₂Cl₂)₃]·9.25CH₂Cl₂ (2b)

$C_{259.25}H_{321.5}Ba_4Cl_{24.5}N_3O_{30}S_{24.5}$, $M = 6147.4$. Cubic, space group $I\bar{4}3d$ (T_d^6, No. 220), $a = 49.409(6)$ Å, $V = 120620$ Å³. D_c ($Z = 16$) = 1.35_4 g cm⁻³. $\mu_{Mo} = 9.6$ cm⁻¹; specimen: $0.25 \times 0.20 \times 0.20$ mm; $T_{min./max.} = 0.88$. $2\theta_{max.} = 55°$; $N_t = 644560$, $N = 11972$ ($R_{int} = 0.10$), $N_o = 8621$; $R = 0.070$, $R_w = 0.078$. $x_{abs.} = 0.08(2)$.

Variata: Included solvent residues were modelled in terms of CH_3CN (ligand 1) and CH_2Cl_2 (ligand 2); lattice residues were modelled in terms of CH_2Cl_2, #3, 5, 7 half-weighted with constrained geometries and isotropic displacement parameter forms, and #4 disordered about the 3-axis. Hydroxylic hydrogen atoms were not located and assignment in the above formula is *ad hoc*, as is the carbonate, presumed to originate in atmospheric carbon dioxide in the basic conditions of the synthesis. Either in consequence of disorder or twinning, the Ba_4 tetrahedron is imaged as its inverse, site occupancies of parent and complement component occupancies refining to 0.920(2) and complement, associated light atom components not being located.

Ga(OH)(LH₂)·3.5dmf (×2) ≡ [{(dmf-*O*)(dmf·LH₂)Ga(μ-*OH*)}₂]-(·3dmf) (3)

$C_{101}H_{143}Ga_2N_7O_{17}S_8$, $M = 2123.3$. Orthorhombic, space group *Ibam* (D_{2h}^{26}, No. 72), $a = 21.369(2)$, $b = 22.416(2)$, $c = 23.431(2)$ Å, $V = 11224$ Å³. D_c ($Z = 4$) = 1.25_7 g cm⁻³. $\mu_{Mo} = 6.9$ cm⁻¹; specimen: $0.57 \times 0.13 \times 0.12$ mm; $T_{min./max.} = 0.73$. $2\theta_{max.} = 50°$; $N_t = 55342$, $N = 4968$ ($R_{int} = 0.076$), $N_o = 3634$; $R = 0.10$, $R_w = 0.12$.

Variata: Dmf molecules 10 (coordinated), 20 (included) were modelled as disordered about the crystallographic mirror plane passing through the pair of gallium atoms, lattice molecule 30 as disordered about a 2-axis; geometries of molecules 20, 30, 40 (the latter also modelled as disordered) were constrained at estimated values and refined with isotropic displacement parameter forms, as also were those of the *tert*-butyl groups, which were modelled as rotationally disordered about their pendant bonds, all associated disordered component site occupancies being set at 0.5. Phenolic hydrogen atoms were not located. The true space group may be of lower symmetry, but, with the present data, is insusceptible of meaningful refinement as such.

In(LH)·4EtOH·CH₂Cl₂ (×2) ≡ [{(EtOH)In(μ-*O*-{HL·CH₂Cl₂})}₂]-(·6EtOH) (4a)

$C_{98}H_{142}Cl_4In_2O_{16}S_8$, $M = 2204.2$. Triclinic, space group $P\bar{1}$, $a = 13.257(2)$, $b = 15.541(2)$, $c = 15.662(3)$ Å, $\alpha = 62.117(2)$, $\beta = 69.506(2)$, $\gamma = 87.540(2)°$, $V = 2643$ Å³. D_c ($Z = 1$) = 1.38_5 g cm⁻³. $\mu_{Mo} = 7.6$ cm⁻¹; specimen: $0.45 \times 0.25 \times 0.08$ mm; $T_{min./max.} = 0.73$. $2\theta_{max.} = 58°$; $N_t = 25734$, $N = 12751$ ($R_{int} = 0.039$), $N_o = 9960$; $R = 0.055$, $R_w = 0.063$.

Variata: Hydrogen atoms were located on the ethanol OH groups and on the uncoordinated (3) phenolic OH group.

In(OH)(LH$_2$)·3CH$_2$Cl$_2$ (×4) ≡ [{In(μ-OH)(μ-O-{H$_2$L·CH$_2$Cl$_2$})}$_4$]-(·8CH$_2$Cl$_2$) (4b)

C$_{172}$H$_{212}$Cl$_{24}$In$_4$O$_{20}$S$_{16}$, M = 4422.8. Tetragonal, space group $I\bar{4}$ ($S_4{}^2$, No. 82), a = 24.150(2), c = 16.864(2) Å, V = 9835 Å^3. D_c (Z = 2) = 1.49$_3$ g cm^{-3}. μ_{Mo} = 10.2 cm^{-1}; specimen: octahedron, ca. 0.35 mm; $T_{min./max.}$ = 0.83. $2\theta_{max.}$ = 69°; N_t = 75947, N = 10077 (R_{int} = 0.048), N_o = 7765; R = 0.082, R_w = 0.097.

Variata: Lattice dichloromethane molecules #3, 4, were modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement; *tert*-butyl 14 is modelled similarly, rotationally disordered about the pendant bond over two sets of sites. No hydrogen atoms could be located in associated with bridging (aqua-derived)-O or ligand phenoxy-O atoms. (See discussion at greater length below).

OPb$_4$(LH)$_2$·6dmf·dmso·2H$_2$O ≡ [(μ$_4$-O){Pb(O-dmf/dmso)}$_2${Pb(O-dmf)(OH$_2$)}$_2$(LH·dmf)$_2$](·dmf) (5)

C$_{100}$H$_{142}$N$_6$O$_{18}$Pb$_4$S$_9$, M = 2833.7. Monoclinic, space group $P2_1/n$ ($C_{2h}{}^5$, No. 14, variant), a = 20.183(1), b = 12.6041(6), c = 24.592(1) Å, β = 112.749(1)°, V = 5769 Å^3. D_c (Z = 2) = 1.63$_1$ g cm^{-3}. μ_{Mo} = 60 cm^{-1}; specimen: 0.25 × 0.15 × 0.08 mm; $T_{min./max.}$ = 0.49. $2\theta_{max.}$ = 68°; N_t = 87844, N = 22879 (R_{int} = 0.055), N_o = 13434; R = 0.072, R_w = 0.075.

Variata: No hydrogen atoms were defined in association with the central residue, assigned as oxo-O, or with the phenoxy-O atoms, charge balance considerations being consistent with a model in which L is incompletely deprotonated [note that O···O distances within the ligand are long (Table S1)], and with a lead oxidation state of 2. Disorder is evident in the solvent ligand bound to the Pb(2), being modelled as 0.5 dmf/0.5 dmso about their pendant oxygen atoms. The included dmf(2) molecule is ordered, but lattice dmfs #4–6 were also modelled with site occupancy factors 0.5 with constrained geometries. A substantial difference map residue was observed ca. 2.3 Å above O(0), together with another closer to Pb(2); site occupancy refinement of both these and Pb(1,2) suggested them to be components of disorder of Pb(1,2) [no associated light atom fragments resolvable – note that associated Pb(1′,2′)···ligand donor atom distances are not totally sensible (Table S6) with a non-disordered model for the latter], site occupancies refining to 0.9255(6) and complement (cf. **4b**).

Supporting Information (see footnote on the first page of this article): Tables S1–S7, giving descriptors of ligand and metal atom geometry.

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