DOI: 10.1002/ejic.200901070

Systematic Structural Coordination Chemistry of *p-tert*-Butyltetrathiacalix[4]arene: Further Complexes of Lanthanide Metal Ions[‡]

Alexander Bilyk,[a] John W. Dunlop,[a] Rebecca O. Fuller,[a] Annegret K. Hall,[a] Jack M. Harrowfield,*[a,b] M. Wais Hosseini,[c] George A. Koutsantonis,[a] Ian W. Murray,[a] Brian W. Skelton,[a] Alexandre N. Sobolev,[a] Robert L. Stamps,[d] and Allan H. White[a]

Keywords: Calixarenes / Rare earths / Solvent inclusion / Solid-state structures

Extension of previous work on the lanthanide(III) ion complexes of *p-tert*-butyltetrathiacalix[4]arene has led to a variety of structurally characterised species containing oxo-, hydroxo- and aqua-ligands presumably derived from water present in the preparative medium, along with the thiacalixarene in various stages of deprotonation. The overall stoichiometry of some species is remarkably complicated due to the presence of simple anions and multiple solvents. Simplest is the binuclear complex $[(\mu\text{-}H_2O)\{Ln(O\text{-}dmf)_2\}_2(HL\cdot dmf)_2]\cdot nS$ (dmf = dimethylformamide) [**1Ln**, Ln = Sm (nS = 2dmf), Eu (nS = 1.5dmf·2MeCN)], also the best-defined of all the arrays studied. The heaviest lanthanides give trinuclear $Ln(OH)_3\cdot 2Ln(LH)\cdot x dmf\cdot yH_2O$ (**2Ln**, Ln = Yb, Lu), while both oxo and hydroxo species are isolable with Eu: trinuclear $Eu_3O(L)(LH)(LH_4)\cdot 13dmf$ (**3**) and tetranuclear $Eu_4O(OH)_2(L)(LH_2)_2(LH_4)\cdot 12dmf$ (**9**), both somewhat atypical species containing uncoordinated thiacalixarene molecules within the lattice. Anion (NO_3, ClO_4) coordination, as in the tri- and tetranuclear species, **4–6Ln**, **9**, **10Ln**, **11Ln**, **12**, seems especially favoured for the lighter lanthanides. In these arrays, the Ln_3 and Ln_4 aggregates are triangular or (quasi-)square-planar, except for $Gd_4O_2(LH_2)_4\cdot 2H_2O\cdot 2MeOH\cdot 2dmf\cdot 3.375CH_2Cl_2$ (**12**), where there is a Z-disposition. Most common is an Ln_3O core, which spans the gamut of Ln in three sets of crystal forms with cells of similar dimensions: for Ln = La...Nd, $Ln_3(OH)(NO_3)_4(LH_2)_2\cdot 4.5dmf$ (**5Ln**) (space group $C2/m$), and Sm...Lu, $Ln_3O(NO_3)(LH)_2\cdot 4H_2O\cdot 2dmso\cdot 2MeCN\cdot 3py$ (**6Ln**) (space group $P2_1/n$), conformity with crystallographic symmetry entails disorder of the Ln atoms; in a further form of lower symmetry Pn, $(pyH)Ln_3O(NO_3)_2(LH)_2\cdot 2MeCN\cdot xH_2O\cdot ydmso\cdot 1.5py\cdot MeOH$ (**7Ln**, Ln = La, Ce), with no imposed crystallographic symmetry, some disorder persists, but none is found in the crystallographically unrelated form of **8Pr**, $Pr_3O(NO_3)(LH)_2\cdot 16H_2O\cdot 2MeCN\cdot 5py$. $Ln_4(OH)(NO_3)_3(L)_2\cdot 8dmf\cdot 2dmso\cdot 3H_2O$ (**10Ln**, Ln = Pr...Gd, previously defined for Nd) has a square-planar Ln_4O array sandwiched between a pair of L ligands, with a similar form found for $Ln_4O(ClO_4)_2(L_2)\cdot x dmf\cdot yH_2O$ (**11Ln**, Ln = La...Nd).

Introduction

In the immediately preceding[1,2] and some earlier publications,[3–8] we have described the results of our efforts to characterise, through structural studies, the solid-state coordination chemistry of the macrocyclic ligand *p-tert*-butyltetrathiacalix[4]arene, LH_4, in its "parent", unfunctionalised form. Broader aspects of this chemistry concerning various derivatives and homologues of this thiacalixarene have been recently reviewed,[9] as has the specific function of (thia)calixarenes and their derivatives as "cluster keepers".[10,11] A remarkable aspect of the coordination chemistry of tetrasulfonylcalix[4]arene, in particular, is the formation, aided by carboxylate coligands, of octanuclear and dodecanuclear "wheel" complexes of the lanthanides[11–13] and, in the present work, we show that the formation of oligonuclear lanthanide complexes is characteristic of the interaction of LH_4 with the complete lanthanide series and that our previous characterisation of the tetranuclear sandwich species Nd_4L_2[5] provides but one example of the several structures which appear to be possible. A feature of this structure which is repeated in most of the present cases is the stoichiometric complexity of the asymmetric unit and, as we have found in our earlier studies,[1–8] there appears to be a complicated kinetic control of the species deposited from the various reaction mixtures, involving solvents such as dimethylformamide (dmf), dimethyl sulfoxide (dmso), acetonitrile and pyridine (py), having a wide range of polarity and basicity, used for synthesis. The lanthanide(III) complexes provide the first instance of an extended set of M^{III} derivatives of LH_4, previous examples involving only

---

[‡] Part IV; part I: ref.[3]; part II: ref.[1]; part III: ref.[2]

[a] Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, Western Australia 6009
[b] Laboratoire de Chimie Supramoléculaire, Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg, 67083 Strasbourg, France
[c] Laboratoire de Chimie de Coordination Organique, Institut Le Bel, Université de Strasbourg, 67000 Strasbourg, France
[d] School of Physics, The University of Western Australia, Crawley, Western Australia 6009

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200901070.

the smaller cations Fe^{III}, Ga^{III} and In^{III}.[1,2] For complexes of water-soluble thiacalix[4]arene derivatives, with Tb^{III} specifically, however, considerable structural information is available.[11,14,15]

Results and Discussion

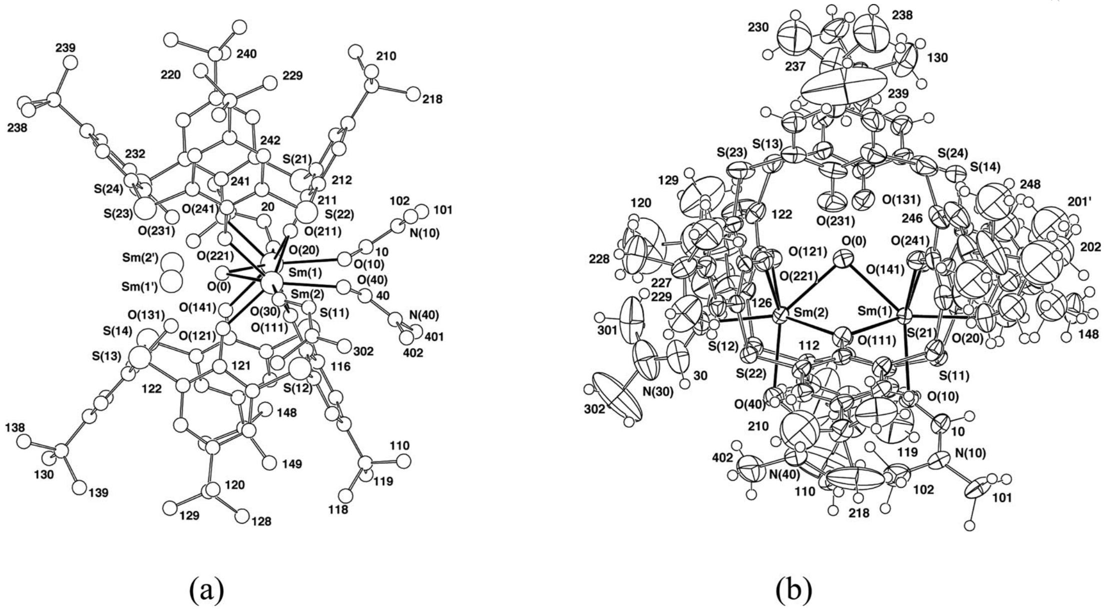
The variety of structures displayed by M^{II} transition-metal complexes of *p-tert*-butyltetrathiacalix[4]arene (see ref.[2,9,11,12] and references cited therein) gives reason to expect a considerable range in spanning the lanthanide (Ln) series. The preparation of crystalline derivatives suitable for structure determinations for fourteen elements (La–Lu, less Pm, plus Y) is a considerable challenge and, despite exploration of several methods of synthesis and crystallisation, it is not possible to report results presently for a full series of complexes, especially one involving a common stoichiometry. A simple method of synthesis which does provide microcrystalline samples for all Ln^{III} is to react dmso solvates of the metal nitrates with the deprotonated ligand in dmso but the products are exceedingly insoluble in most solvents and, although they can be recrystallised from pyridine by vapour-diffusion addition of acetonitrile, this has not in all cases provided crystals suitable for structure determination, and it is clearly associated with changes in the chemical composition of the solids. Various related procedures have proved successful in particular cases, though the consequences of varying reagent concentration, for example, have proved somewhat erratic; more general aspects of the synthesis of thiacalixarene complexes have been discussed earlier,[1,2] including the fact that, despite the use of formally anhydrous reagents, many isolated materials proved to be hydrolysis products from water present in the solvents. Many of the problems associated with attempted single-crystal studies of calixarene complexes, such as their facile efflorescence and disorder associated with *tert*-butyl groups, are well known (see, for example, references[16–18]) and other particular problems in the structure analysis, such as ambiguity in proton locations and the identification of remarkable mixtures of solvent components, have been of considerable importance in the present work. Nonetheless, the results obtained have exposed some fascinating subtleties of lanthanide chemistry, discussed already to a limited extent elsewhere.[10,16d]

The results of the single-crystal X-ray structure determinations are consistent with the gross metal and ligand stoichiometries as given below. However, in general, hydrogen atom assignments were not verifiable by refinement of $(x,y,z,U_{iso})_H$ and their locations are inferred from considerations of geometries, charge balance and other factors, which, in the context of other hydroxylic components and, sometimes, serious disorder, particularly in the presence of solvent components, may not be as secure as desirable. Initially, in order to assist understanding, we approach the complexes in order of increasing complexity/nuclearity and focussing on their description, beginning with the examples of the sole binuclear form, the different types identified being designated by the numbers **1**–**12**. Projections of individual molecules or aggregates are given in the Figures. Metal atom environments are given in the Tables (Supporting Information), as in the preceding Parts II and III,[1,2] Table S1 summarising ligand descriptors which provide some basis for the deduction of the ligand conformation and protonation patterns, while Table S2 provides comparisons of sulfur-atom geometry. Where members of "isomorphous" families have been studied, values for the extremal members studied only are presented in the tables.

$Ln_2(LH)_2\cdot H_2O\cdot 6dmf\cdot nS \equiv [(\mu\text{-}H_2O)\{Ln(O\text{-}dmf)_2\}_2(HL\cdot dmf)_2](\cdot nS)$ (1Sm, 1Eu) {$nS = 2dmf$ (Sm), 1.5dmf·2MeCN (Eu)}

The core of this complex, of a form known so far only for Sm and Eu and for which a neutral molecule, devoid of crystallographic symmetry in a chiral space group, comprises the asymmetric unit of the structure, is an isosceles triangle formed by an oxygen atom of a water molecule, O(0), and a pair of lanthanide atoms. Two macrocycle ligands, assigned as triply deprotonated (Table S1), and with included dmf molecules, lie to either side of this plane, the oxygen atom of the water molecule lying close to the axis passing through their centres, so that the distances to their phenoxide oxygen atoms are closely similar [O(0)···O(1*m*1) (*m* = 1–4) 2.762(9), 2.653(10), 2.676(10), 2.948(9), O(0)···O(2*m*1) 2.751(9), 2.903(11), 2.661(10), 2.715(10) Å, for (e.g.) the Sm complex]. The metal atoms are further bridged by ligand O(*l*11), with further interactions from the phenoxy-*O* to either side [O(*l*21,*l*41)] together with the intervening sulfur atoms [S(*l*1,*l*2)], the unsymmetrically coordinated OS(O-μ) triads from the ligands occupying sets of *fac* sites in the Ln coordination spheres, which thus are nine-coordinate, comprising $[OS(O\text{-}\mu)]_2[\mu\text{-}O(H_2)](O\text{-}dmf)_2$ arrays (Figure 1, Table S3). In **1Sm**, O(111)···O(211) is 2.939(8) Å, slightly longer than the pair of O(0)···O(*l*11) distances above, so that these three atoms also form an isosceles triangle, quasi-normal to the $Ln_2O(0)$ triangle (interplanar dihedral angle [88.3(2)°]. One (phenoxide-)*O*···*O* distance within each ligand is shorter than the others [O(131)···O(141); O(221)···O(231); Table S1] and presumed to contain the last protonic hydrogen, surmised to be associated with the uncoordinated O(*n*31). The contacts O(0)···O(*l*31) also may be surmised to contain hydrogen-bonds arising from the water molecule, assisting to maintain the quite symmetrical sandwich form of the complex.

An intriguing feature of the array, found only in the Sm complex, is the observation of significant difference map residues Sm(1′,2′), imaging Sm(1,2) as quasi-inverses through O(0) and thus quasi-coplanar Sm_2OSm_2', [O(0) lies 0.001(8)] Å out of the $Sm_2Sm'_2$ plane, which have been refined as such, giving occupancies for Sm, Sm′ of 0.940(1) and complement. A similar result was obtained on an independent specimen. The occupancies of the latter sites are



(a) (b)

Figure 1. Projections of the binuclear array of [(μ-H_2O){Sm(*O*-dmf)$_2$}$_2$(HL·dmf)$_2$](·2dmf) (**1Sm**) (the molecule **1Eu** being similar, except that no core disorder is found): (a) The core, showing the location of the minor Sm components vis-à-vis the ligands; (b) down the "line" through the calix centroids and O(0) (the included dmf molecules and minor Sm components are not shown). For **1Sm**, Sm(1,2)–O(0) are 2.515(3), 2.530(2); Sm–O(dmf) are 2.422(3)–2.491(3) Å. Within the OS(O-μ) tripods, Sm–S are 2.973(1)–3.091(1), Sm–O(μ) are 2.411(2)–2.510(2) and Sm–O(non-μ) are 2.287(3)–2.394(3); Sm···Sm is 3.7203(4) Å.

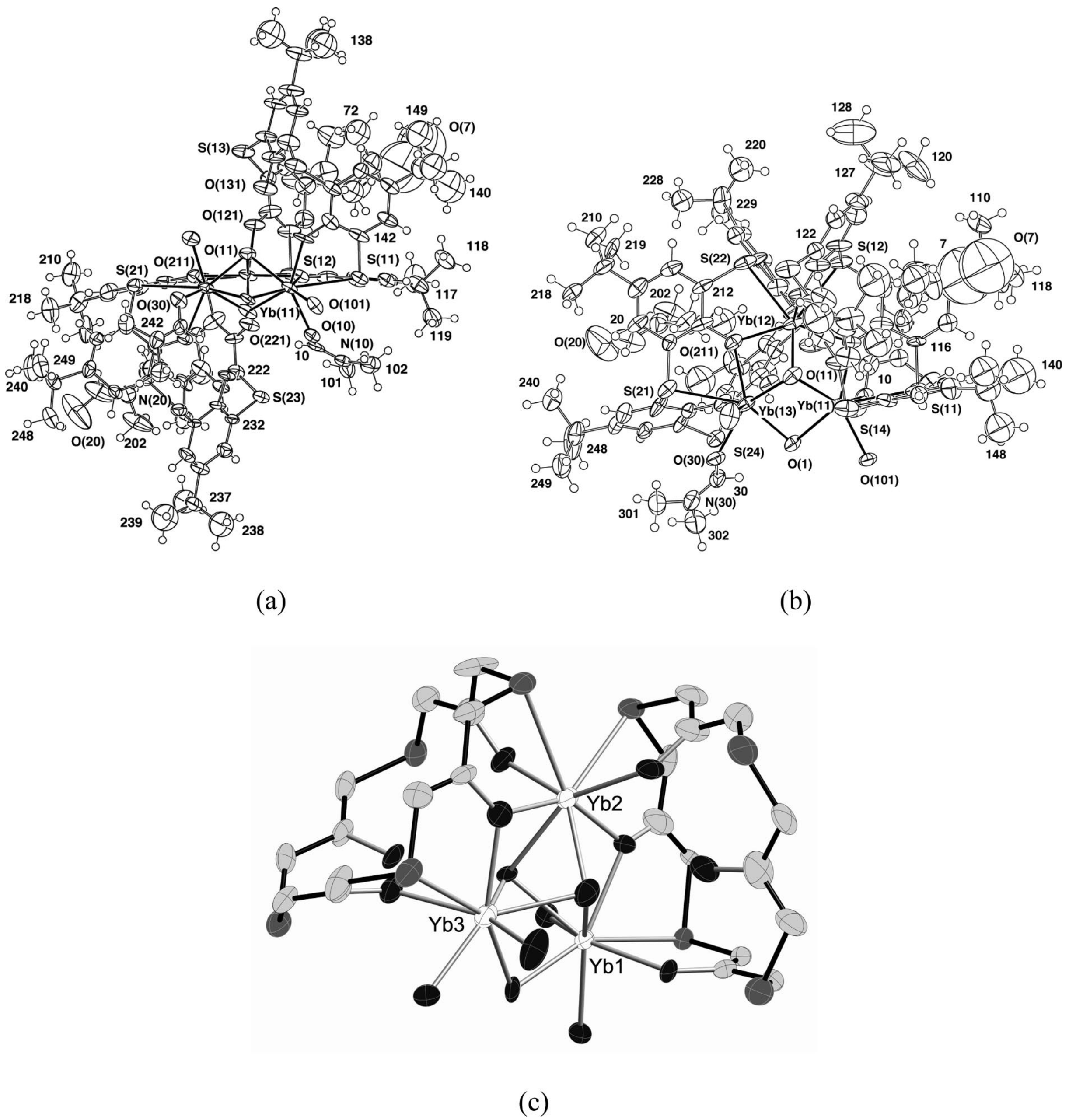
such that it is not surprising that further independent associated light atom residues have not been resolvable in association with them. However, a not unreasonable hypothesis is that the array is a cocrystallised mixture of a parent array as described, with a minor component in which the ligands encapsulate Sm′ fragments rather than Sm; minor ligand displacement to accommodate this has not been resolved, but it is of interest [Tables S3(c,d)] to observe that the essentials of the coordination environments corresponding to those found for the Sm_2 array may be discerned for an array in which the Sm_2 are supplanted by Sm'_2. While little store can be set by the associated geometries in detail, it is of interest to note that the distance Sm(1′)···Sm(2′) [3.15(2) Å] is somewhat shorter than Sm(1)···Sm(2) [3.7203(7) Å], suggesting that the $Sm_2{}'$ array may be associated with a different isomer, perhaps with a different protonation pattern, rather than, e.g., a simple "rotamer" of the parent array, or perhaps even with the presence of some Sm_4O species as described ahead. While the O_4 arrays are quite closely planar, the sulfur atom deviations from their associated O_4 planes (Table S1, Supporting Information) vary widely.

In a lattice in which the molecules pack discretely within columns parallel to *b*, one sandwich complex confronts others at either end, with slightly offset positioning of the outer rims of the calixarene cavities allowing both included dmf molecules to come into CH···O contacts (C···O $\approx$ 3.5 Å) with *tert*-butyl CH_3 groups of their neighbours. The remaining dmf molecules appear to be involved in various weak interactions leading, along with intermolecular *tert*-butyl-CH_3···π attractions, to the assembly of the complete lattice, as seen in other systems already described.[1–8] Adjacent coordinated dmf molecules may also be involved in weak mutual attraction [O···C(formyl) 3.12(1) Å].

Ln(OH)$_3$·2Ln(LH)·*x*dmf·*y*H_2O ≡ [(HO)$_3${Ln(OH$_2$)}$_2$-{Ln(*O*-dmf)}(HL·dmf)$_2$][·(*x* – 3)dmf·(*y* – 2)H_2O], Ln = Yb, Lu, (2Ln)

For these smaller rare earths terminating the heavy end of the series, a trinuclear cluster which differs from the array of **3** is found (Figure 2, Table S4). Its core is an Ln_3 array, with geometry close to that of an equilateral triangle in spite of gross differences in the core- and peripheral environments about the three Ln atoms which degrade the overall symmetry of the array in each of the two similar molecules of the asymmetric unit of each structure to quasi-2. Three oxygen atoms associated as bridges with each Ln_3 core are assigned as OH groups; two bridge the three Ln above and below the plane at similar distances and with almost identical Ln–O–Ln angles, the third bridging two [Ln(1,3)] in-plane symmetrically [Figure 2, (a)]. The "out-of-plane" OH groups differ in their deviations from the Ln_3 plane by ca. 0.05 Å [Table S4, (d)], with the deviation of the "in-plane" OH group also significant (ca. 0.1_7 Å). The median plane of the molecule is made up to a quasi-symmetrical $O_2Ln_3O_3$ array by the incorporation of two further in-plane bridging oxygen atoms, O(*l*11) phenoxy-*O* atoms from the two ligands *l* = 1,2, none of which deviate from the Ln_3 plane by more than 0.21 Å; with the sulfur atoms to either side these make up an S(O-μ)S near-planar tridentate array, quasi-coplanar with the Ln_3O_3 array, linking to the two Ln bridged by the central oxygen. The remainders of the two macrocycles are largely disposed one to each side of the core plane, O(*l*41) contributing to *fac*-OS(O-μ) tridentates about Ln(1,3), while O(*l*21) contribute likewise about Ln(2). The "central" Ln(2) environments thus comprise a pair of OS(O-μ) *fac*-tripod tridentate contributions from the two macrocycles, unsymmetrically bound, together with a pair of μ-OH groups above and below the core plane, and are thus eight-coordinate.

The "peripheral" Ln, Ln(1,3) are also eight-coordinate, having three bridging hydroxo groups, an unsymmetrical tridentate OS(O-μ) *fac*-tripod interaction from one of the macrocycles, and a pair of unidentate *O*-donors (water and dmf). The disposition of these is curious – on Ln(1), the



(a) (b)

(c)

Figure 2. Projections of molecule 1 of $[(HO)_3\{Yb(OH_2)\}_2\{Yb(O\text{-}dmf)\}(HL\cdot dmf)_2][\cdot(x-3)dmf\cdot(y-2)H_2O]$ (≡ 3dmf·4H_2O) (**2Yb**) (as representative of **2Ln**): (b) Oblique and (b) normal to the Yb_3 plane (without the included dmf molecules). For **Yb2**, Yb(*l*1,*l*3)–O(*l*) are 2.260(7)–2.280(7); Yb(*l*1,*l*3)–O(*l*1,*l*2) are 2.279(8)–2.374(10); Yb(*l*2)–O(*l*1,*l*2) are 2.287(9)–2.319(9) Å (molecules *l* = 1,2). About Yb(*l*2), in the OS(O-μ) tripods Yb–S are 2.891(3)–2.909(3), Yb–O(μ) 2.268(7)–2.304(10), Yb–O(non-μ) 2.209(9)–2.270(9) Å. About Yb(*l*1,3), Yb–O(dmf) are 2.266(9)–2.341(2) and Yb–O(H_2) 2.280(11)–2.338(11) Å; in the OS(O-μ) tripods, Yb–S are 2.955(4)–3.002(3), Yb–O(μ) 2.319(8)–2.350(8) and Yb–O(non-μ) 2.333(2)–2.362(3) Å. Yb(*l*2)···Yb(*l*1,*l*3) are 3.428(1), 3.439(1); Yb(*l*1)···Yb(*l*3) are 3.434(1), 3.446(2) Å. (c) A perspective view of the core of the trinuclear complex, only the macrocyclic ring atoms (and their attached oxygen atoms) of the calixarene being shown.

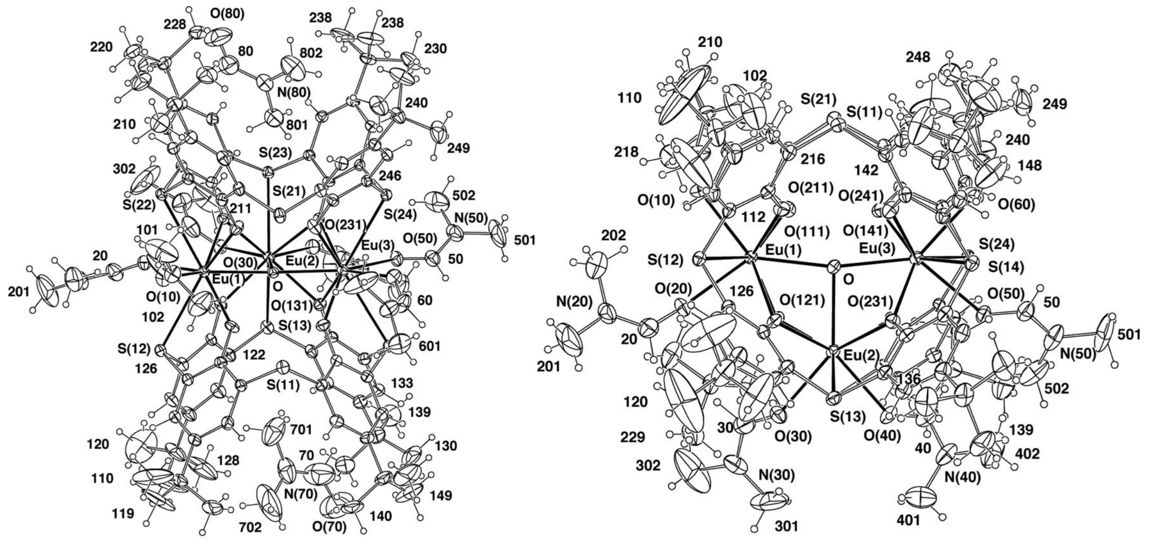
water molecule lies in the median plane and the dmf-*O* out, a situation which is reversed on Ln(3), breaking the overall quasi-2 symmetry of the rest of the array. The origin of this difference may lie in intermolecular hydrogen-bonding: O(1)···O(201) is 2.74(2) and O(2)···O(101) 2.60(2) Å, suggesting a pairing of the two independent molecules of the asymmetric unit as a quasi-centrosymmetric dimer. Within each macrocycle, there is only one short O···O distance, consistent with the postulation of triple-deprotonation; each macrocycle has an included dmf.

$Eu_3O(L)(LH)(LH_4)\cdot 13dmf \equiv [O\{Eu(O\text{-}dmf)_2\}_3(L\cdot dmf)(HL\cdot dmf)][H_4L\cdot dmf]\cdot 4dmf$ (3)

Like **2Ln**, **3** contains an OLn_n medial planar array bound together into the aggregate by a pair of macrocycle ligands to either side, the central oxygen atom lying 0.087(3) Å out of the Eu_3 plane, and quasi-equidistant from the Eu (Figure 3; Table S5). In ligand 1, all O···O distances are large enough to be consistent with complete deprotonation, while in ligand 2, r_{14} is short, consistent with a residual proton as written (Table S1). An uncomplexed ligand is also found in the structure [Figure 3, (b)], some O···O distances within it sufficiently large to be consistent with some degree of deprotonation (Table S1); ad hoc, it is modelled in the formula as fully protonated but there may be some transfer to, e.g., the oxo-oxygen atom. The cone of the ligand is remarkably unsymmetrical (Table S1), with wide variations in the deviations of the sulfur atoms from the O_4 plane, more so than in the coordinated ligands, which are unsymmetrically disposed about the Eu_3 triangle. The presence of free ligand within the lattice appears, so far as is presently known, to be confined to Eu^{III} complexes but its explanation is obscure. All ligands contain included dmf; each europium atom carries a pair of dmf ligands coordinated in the median plane, while four, with high displacement amplitudes, are found in the lattice. One formula unit, a single trinuclear molecule, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure.

The Eu_3 triangle is isosceles, Eu(2) at the apex, with Eu(1)–O–Eu(3) 166.66(6)° and Eu(2)–O–Eu(1,3) 96.06(4), 96.38(4)°; Eu(2)–O is slightly longer than Eu(1,3)–O. Each ligand provides three OSO tripod/*fac* approaches, to each of the three Eu atoms, those from the outer Eu(1,3) being unsymmetrical OS(O-μ) and from the central $S(O\text{-}\mu)_2$. The coordination environments of the peripheral Eu(1,3) atoms are thus $[OS(O\text{-}\mu)]_2O(O\text{-}dmf)_2$, while that of the central [Eu(2)] is $[S(O\text{-}\mu)_2]_2O(O\text{-}dmf)_2$, all nine-coordinate (Table S5). The gross symmetry of the aggregate is quasi-2*m* but the two ligands differ in respect of O···O distances (Table S1): in ligand 1, all four are greater than 3.1 Å, whereas in ligand 2, one [straddling the vertical quasi-mirror plane, adjacent to the central oxygen atom (Table S5)] is as short as 2.653(5) Å, consistent with the deprotonation pattern ascribed in the formula.

Viewed down *a*, the lattice appears to be built up from columns of complex units parallel to *a* (though the perpendicular to the Eu_3 plane is not parallel to *a*), with the centres of these columns defining parallelograms of two different sizes such that alternating layers parallel to *ab* of all less- and all more-flattened parallelograms define the projection seen. Diagonally arrayed across the larger (less flattened) parallelograms are pairs of "free" calixarene molecules, as their dmf inclusates, appearing side-by-side as "one



(a) (b)

Figure 3. Projections of the complex molecule $[O\{Eu(O\text{-}dmf)_2\}_3(L\cdot dmf)(HL\cdot dmf)][H_4L\cdot dmf]\cdot 4dmf$ (**3**): (a) Oblique to the Eu_3 plane and (b) normal to the Eu_3 plane (without the included dmf molecules). O–Eu(2,1,3) are 2.411(1), 2.396(1), 2.387(1); Eu(2,1,3)–O(dmf) are 2.407(2), 2.415(1), 2.419(2)–2.506(1) Å. Within the $S(\mu\text{-}O)_2$ tripods about Eu(2), Eu–S are 2.9583(5), 3.0009(5), Eu–O(μ) 2.392(1)–2.412(1); within the OS(O-μ) tripods about Eu(1,3), Eu–S are 2.9943(5)–3.0861(5), Eu–O(μ) 2.398(1)–2.430(1), Eu–O(non-μ) 2.263(1)–2.464(1); Eu(2)···Eu(1,3) are 3.5738(2), 3.5758(3), Eu(1)···Eu(3) 4.7501(2) Å.

up, one down". These, of course, also form columns parallel to *a*. While there is a superficial resemblance of the array of the free ligand molecules in these columns to those seen in lattices of the solvated ligand itself,[3,16a] the array is much more open, involving no contacts indicative of π-stacking and only some rather remote $CH_3\cdots CH_3$ and $CH_3\cdots C$(aromatic) approaches ca. 3.8 Å. Once again it seems that dmf, included, coordinated and "lattice" serves, through $CH_3\cdots O$, $\cdots CH_3$(*tert*-butyl) and $\cdots$C(aromatic) distances of 3.5–3.8 Å, to provide the principal means of direct contact between the various lattice moieties, including that leading to slightly offset confrontation of cavities of calixarenes on adjacent complex units in the columns parallel to *a*.

$Eu_6O_2(NO_3)(LH)_3(L)\cdot$dmso$\cdot$5MeCN$\cdot$11dmf$\cdot$4.75$H_2O$ ≡ [O{Eu(*O*-dmf)(NCMe)}{Eu(ONO$_2$)(*O*-dmf)}{Eu(*O*-dmf)$_2$(HL·NCMe)$_2$}][O{Eu(*O*-dmf)$_2$}{Eu(*O*-dmf)(*O*-dmso)}{Eu(*O*-dmf)(NCMe)}(HL·NCMe)(L·NCMe)](·3dmf·4.75H_2O) (4)

Although more complicated, this complex closely resembles, in most respects, the arrays of 2 and 3, with a trinuclear isosceles triangular (O)Eu_3 core in each of the two presumably neutral "molecular" aggregates of the asymmetric unit, and a pair of largely deprotonated [as evidenced by their O···O distances (Table S1)] macrocycle units to either side of each OEu_3 plane, and linking the europium atoms, all nine-coordinate, in similar fashion, by chelation

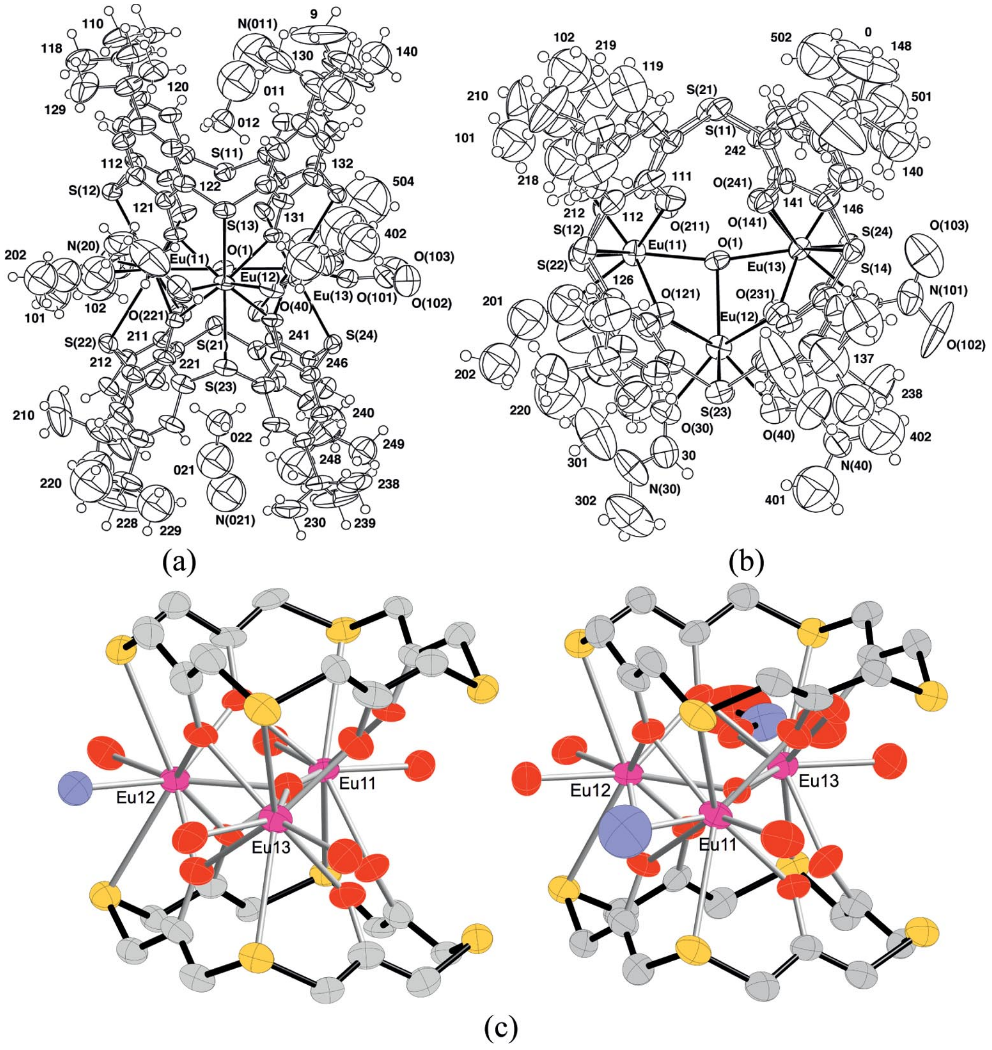


Figure 4. Projections of the first component of [O{Eu(*O*-dmf)(NCMe)}{Eu(ONO$_2$)(*O*-dmf)}{Eu(*O*-dmf)$_2${(HL·NCMe)$_2$}][O{Eu(*O*-dmf)$_2$}{Eu(*O*-dmf)(*O*-dmso)}{Eu(*O*-dmf)(NCMe)}(HL·NCMe)(L·NCMe)](·3dmf·4.75H_2O) (**4**): (a) Oblique and (b) normal to the Eu_3 plane (without included MeCN). [Component 2 is closely similar, except for changes in the unidentate ligand array about Eu(m3).] (Across the two similar components, m = 1,2): O(m)–Eu(m2,m1,m3) are 2.433(4), 2.454(4); 2.366(5)–2.420(4); Eu(m2)–O(dmso) are 2.370(5)–2.429(5); Eu(22)–N(MeCN) 2.410(5); Eu(m1,m3)–O(dmso) are 2.363(6)–2.491(5); Eu(11)–N(MeCN) is 2.388(8); Eu(13)–O(nitrate) is 2.476(5) Å. Within the S(μ-O)$_2$ tripods about Eu(m2), Eu–S are 2.958(2)–3.005(2), Eu–O(μ) 2.379(4)–2.423(5); within the OS(O-μ) tripods about Eu(m1,m3), Eu–S are 2.970(2)–3.094(2), Eu–O(μ) 2.398(5)–2.446(6), Eu–O(non-μ) 2.285(4)–2.541(5) Å. Eu(m2)···Eu(m1,m3) are 3.579(1)–3.605(1); Eu(m1)···Eu(m3) are 4.692(1), 4.766(1) Å. (c) Comparison of the closely similar coordination cores of the two species present in the lattice (C = grey, N = blue, O = red, S = yellow, Eu = pink).

and bridging (Figure 4; Table S5). The central oxygen atoms lie 0.06(1), 0.13(1) Å out of the relevant Eu_3 planes; the distances to the pair of basal Eu(1,3) atoms here are conspicuously shorter cf. those to Eu(2) than in 3 (Table S6), although other dimensions of the OEu_3 arrays are similar.

"Molecule 2" has an O···O distance array similar to that found in **3** and is ascribed as neutral due to a similar ligand protonation pattern (Table S1). In "molecule 1", there are short O···O distances in both ligands (Table S1), the additional proton compensating for the presence of the nitrate group. Pairs of solvent residues, assigned as water molecule oxygen atoms O(01, 02), lie at hydrogen-bonding distances from the core OEu_3 oxygen atoms, O(1)···O(01) and O(2)···O(02), being 2.78(2), 2.79(2) Å, and in-plane [δO(01,02) from Eu_3: 0.06(1), 0.14(2) Å], so that they are essentially "included" between the ligands, with O(01)···O(1111,1141,1211,1241), S(111,121) 2.23(3), 2.51(2), 2.45(2), 2.45(3), 3.02(3), 3.08(3) and O(02)···O(2111,2141,2211,2241), S(211,221) 2.31(3), 2.58(2), 2.55(2), 2.59(3), 2.87(2), 3.17(2) Å.

Again viewed down *a*, there is a striking similarity of the lattice of **4** to that of **3**, despite the fact that no "free" ligand is present in this solid. The complex unit columns parallel to *a* in fact consist of homogeneous components. Here, four columns of complex units enclose a column (parallel to *a*) of water molecules hydrogen-bonded amongst themselves (see above) as well as possibly to NCH_3 of coordinated dmf (C···O ≈ 3.7 Å). The lattice dmf is broadly distributed and, along with coordinated dmf, again appears to make a variety of contacts supporting the overall structure. Partial confrontation of calixarene cavities is associated with a remote contact (≈ 3.7 Å) of the nitrogen atom of the included acetonitrile to a *tert*-butyl methyl–carbon atom of an adjacent complex. Without superior data enabling refinement of phenolic and hydroxylic proton locations in particular, some uncertainty must remain regarding details of the differences between **3** and **4**.

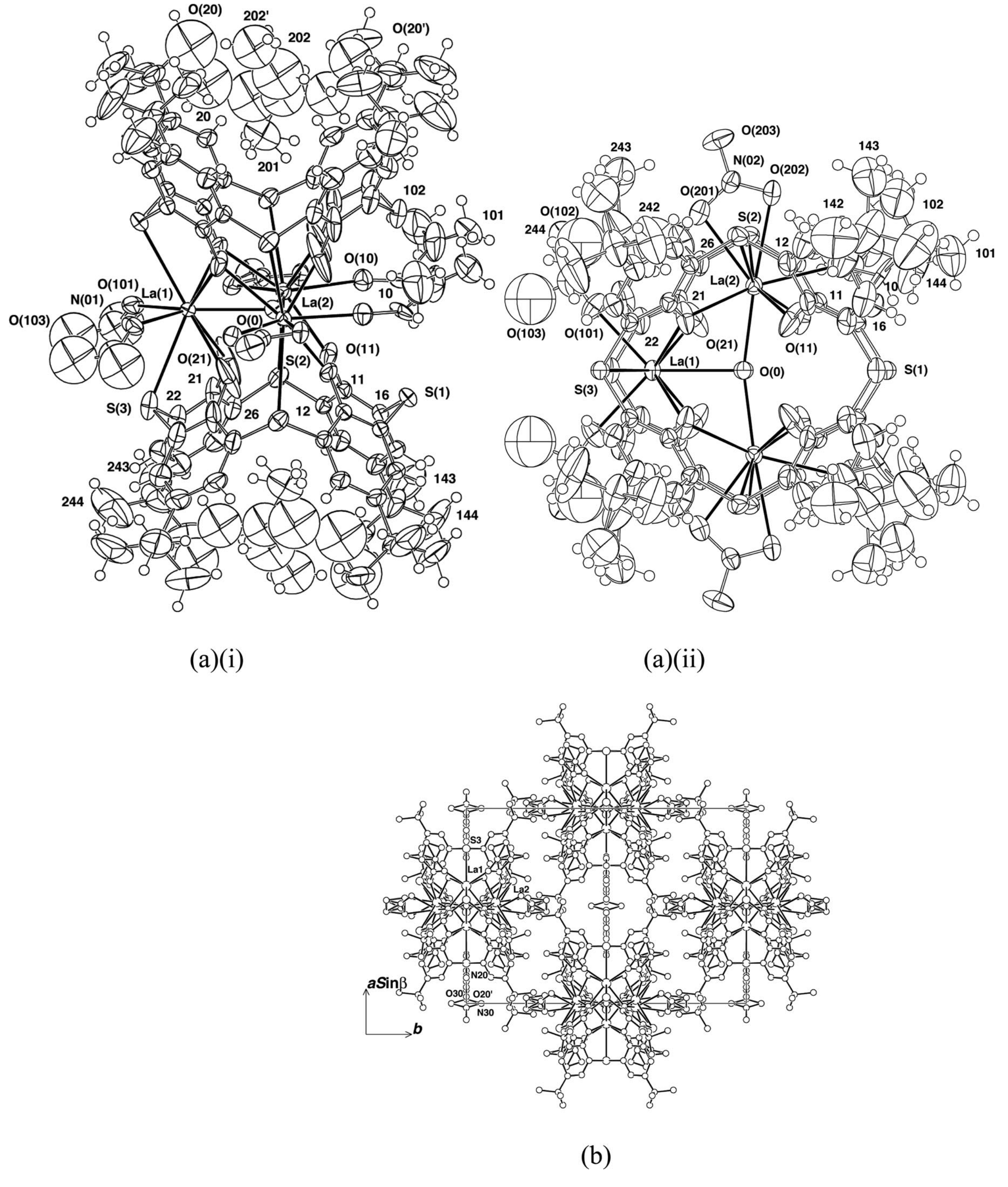
$Ln_3(OH)(NO_3)_4(LH_2)_2\cdot4.5dmf \equiv [(HO)\{Ln(ONO_2)_2\}\{Ln(\mathit{O}NO_2)(\mathit{O}\text{-}dmf)\}_2(H_2L\cdot dmf)_2](\cdot0.5dmf)$ (Ln = La, Ce, Nd) (5Ln)

These three compounds, obtained for La, Ce, Nd and presumed accessible for at least Ln = Pr, crystallise such that one quarter of the presumedly neutral molecular aggregate comprises the asymmetric unit of the structure in space group *C*2/*m*, with some uncertainty in the distribution of the protonic hydrogen atoms. The array is otherwise similar to that of complex **2**, except that, at each of the peripheral lanthanide atoms, one of the dmf groups of **2** is replaced by a bidentate nitrate group, while at the central both dmf molecules are replaced by unidentate nitrates; the latter are badly disordered and conceivably could be NO_3/dmf composites, which would assist the description of the central OH as O, as in **2**, although the calixarenes would then require higher levels of protonation than two. **5La** is depicted in Figure 5; geometries for the Ln = La, Nd extrema are given in Table S7 (Supporting Information). The complex unit of the trinuclear species has an effective mirror plane perpendicular to the $Ln_3O(H)$ plane, passing through the Ln(1)–O(0) vector. The central Ln [Ln(1)], with two unidentate nitrate ligands, is nine-coordinate in an O_7S_2 environment [involving two $S(O\text{-}\mu)_2$ *fac*-tripods], the two flanking Ln(2) having chelating nitrate and unidentate dmf donors, the coordination spheres being completed by the central oxide/hydroxide and donors from the two calixarenes, which both act as heptadentate O_4S_3 ligands (three linked OSO *fac*-tripods, two OS(*O*-μ) and one S(*O*-μ)$_2$ (common *O*-μ), so that both Ln(2) are ten-coordinate in O_8S_2 environments. Despite the same denticity and very similar quasi-*cone* conformations (with dmf inclusion), the two calixarene ligands are not equivalent, there being in particular a much greater asymmetry and bond length differences in the phenoxide-bridging of Ln(1) and Ln(2) by one than by the other [e.g. for Ln = La, La(1)–O(11) 2.454(5), La(2)–O(11) 2.472(4) Å, cf. La(1)–O(21) 2.676(8), La(2)–O(21) 2.809(6) Å]. For the lattice viewed down the *ac* diagonal, the complex units appear to lie in columns parallel to this vector but with the Ln_3 planes slightly tilted from it, resulting in offset confrontation of the dmf-filled calixarene cavities. Intermolecular contacts here appear to be limited to *tert*-butyl $CH_3\cdots CH_3$ (≈ 3.7 Å), the dmf molecules being buried to the extent that the carbonyl-*O* atoms have possible O···HC interactions involving the methyl groups of their own cavities and not the other. Interactions between complex units in adjacent columns appear to involve approaches of the *tert*-butyl methyl groups to both aromatic carbon and to oxygen of coordinated nitrate.

With the introduction of pyridine (py) as ligand (a result of the fact that boiling pyridine was the only solvent found to dissolve the initial precipitates from the synthesis mixture), the related **6Ln**, **7Ln**, **8** are obtained:

$Ln_3O(NO_3)(LH)_2\cdot4H_2O\cdot2dmso\cdot2MeCN\cdot3py \equiv [O\{Ln(\mathit{O}\text{-}dmso)(py)\}_2\{Ln(OH_2)(ONO_2)\}(HL\cdot NCMe)_2](\cdot py\cdot3H_2O)$ (Ln = Sm, Eu, Dy, Lu) (6Ln)

Despite a grossly different anion and solvent component, compounds **6Ln** crystallise in a similar unit cell to that of **5Ln**, at least in respect of dimensions (Figure 6), the pyridine components presumably in terms of symmetry, size and planarity being not too different from the nitrate groups which they replace, charge balance presumably being maintained by change in the protonation pattern of the macrocycles. The present array is defined (thus far) for the lanthanides for a domain from samarium onwards (Table S8, Supporting Information), presumptively accessible by intermediate Ln, as well as Y; the heavy extremum for the series **5Ln** terminates (thus far) at neodymium, but might be considered to be extended fully through the series by this



(a)(i)

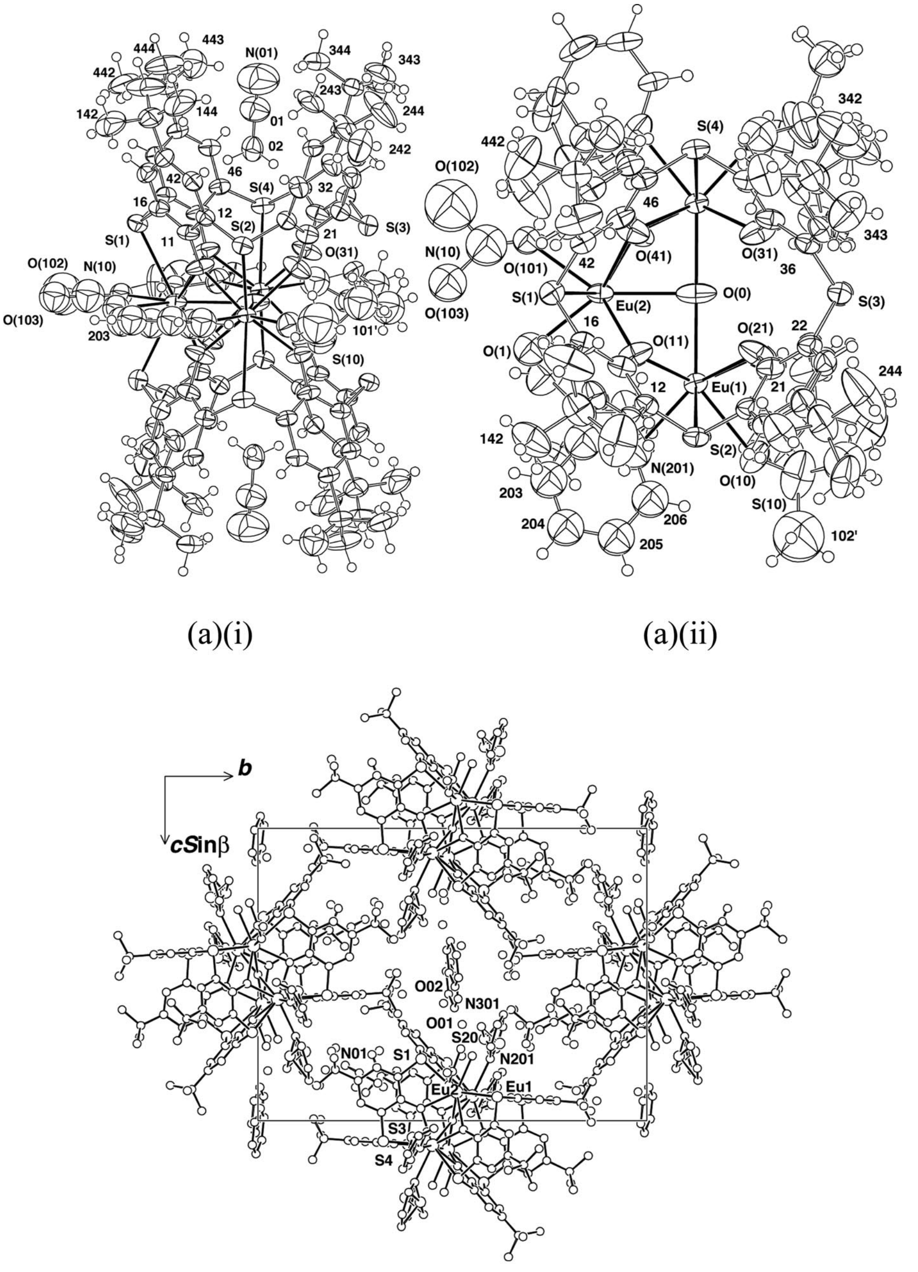
(a)(ii)

(b)

Figure 5. (a) Projections of the complex molecule of $[(HO)\{Ln(ONO_2)_2\}\{Ln(ONO_2)(O\text{-dmf})\}_2(H_2L{\cdot}dmf)_2](\cdot 0.5dmf)$ (**5La**) (as representative of **5Ln**) (a)(i) oblique and (a)(ii) normal to the La_3 plane (without included dmf). The array is of *m* symmetry, *m* through Ln(1,3), S(1,3), the included dichloromethane (disordered) and O(30) of the dmf (pendant atoms also disordered, about the mirror plane). (b) Unit cell contents, projected down *c* (*C*2/*m* symmetry).

similar array. Caveats over cell and space group assignments are exposed in the Experimental Section, yet the dispositions of the complex aggregates within the cells make sense within the symmetries assigned, the aggregate orientation within the cell of **5Ln** aligned in conformity with *C*2/*m* even if the Ln_3 disposition within that cannot be, in any ordered structure, while in **6Ln** the array is canted sufficiently that conformity to *2*/*m* symmetry must be lost, only *i* remaining. Viewed down *a*, the lattice appears to be made up of layers of complex units in planes parallel to *c*, with a tilt of the axis perpendicular to the Sm_3 planes of each complex unit of ±30° relative to *b* alternating from one plane to the next.

The polar mid-sections of the sandwich complexes form the wider boundaries of a column of oval cross-section running through the array parallel to *a* which is filled by pyridine and water molecules (those not in the primary coordination spheres of the metals). These solvent molecules interact separately with coordinated ligands, pyridine being hydrogen-bonded to water (N···O ca. 3.13 Å) and water to nitrate (O···O ca. 3.31 Å), while pyridine also appears to be involved in edge-to-edge interactions with another pyridine adjacent in the column. The orientation of a complex unit in one plane to its nearest neighbour in another is not such as to bring the calixarene cavities into confrontation but instead brings included acetonitrile-*N* into contact with Eu-ligand atoms.



(a)(i)

(a)(ii)

(b)

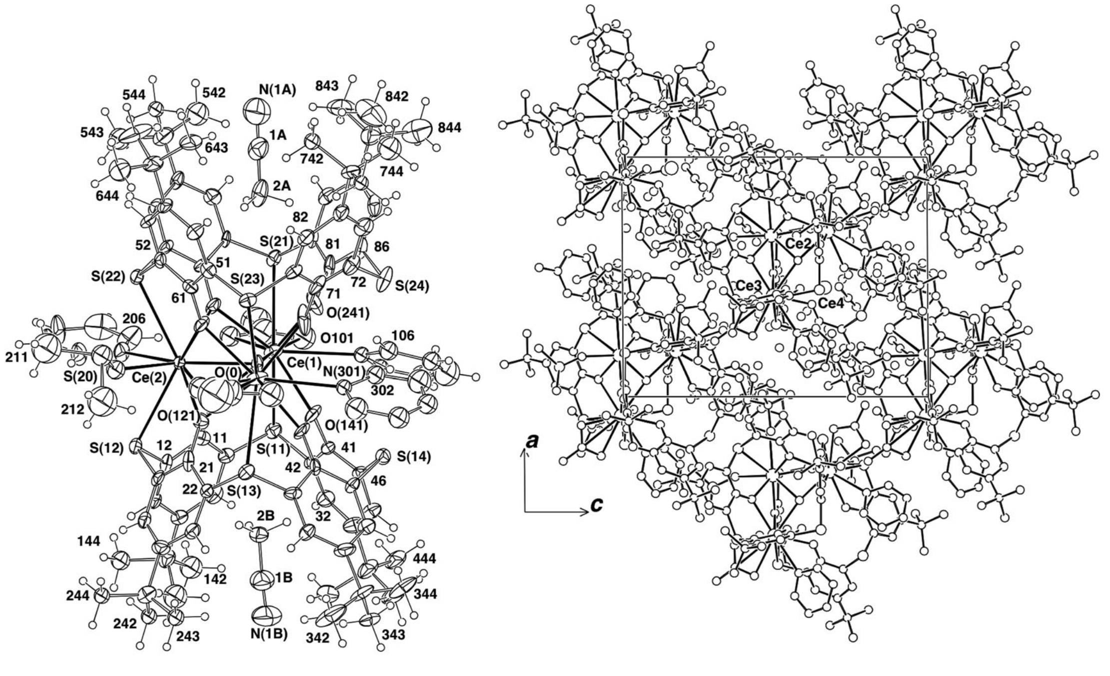
Figure 6. (a) Projections of the complex molecule of $[O\{Ln(O\text{-dmso})(py)\}_2\{Ln(OH_2)(ONO_2)\}(HL\cdot NCMe)_2](\cdot py\cdot 3H_2O)$ (**6Eu**) (as representative of **6Ln**) (a)(i) oblique to the Eu_3 plane and (a)(ii) normal to the Eu_3 plane without included MeCN. (b) Unit cell contents, projected down *a* ($P2_1/n$ symmetry) [cf. Figure 5, (b)].

$(pyH)Ln_3O(NO_3)_2(LH)_2 \cdot xH_2O \cdot y$dmso·2MeCN·1.5py·MeOH ≡ $(pyH)_{(2|2)}[O\{Ln^a(O_2NO)(py)_{0.5}\}\{Ln^bL^x\}$-$\{Ln^c(O_2NO)(py)_{0.5}\}\{Ln^d$(*O*-dmso)$_yL^y\}(HL \cdot MeCN)_2] \cdot xH_2O$ (Total Population $Ln^{a,b,c,d} = 3$) [Ln = La, L^x = MeOH, L^y = (0.5py + 0.5dmso), *x* = 3, *y* = 1.5; Ln = Ce, *b* = 0, L^x = *O*-dmso, L^y = MeOH, *x* = 2, *y* = 1] (7Ln) (Ln = La, Ce)

The descent in symmetry, from *C*2/*m* for the arrays of **5Ln**, through *P*2_1/*n* for **6Ln**, continues with the present **7Ln** array being defined in space group *Pn*, the relationship being clearly implied in the ability to initially model the structures in space group *P*2_1/*n*, refinement therein terminating unsatisfactorily at residuals above 0.15. In **5Ln** and **6Ln**, disorder was coupled with the intrinsic symmetry of the space group; here there is no such association, the full formula unit devoid of crystallographic symmetry comprising the asymmetric unit of the structure (Figure 7).

Despite the lack of crystallographic symmetry, disorder of the lanthanide core persists, though very differently in the two members defined (Ln = La, Ce; Table S9), perhaps consequent on the difference in their atomic radii, perhaps on the difference in the ligated species, a number of which are modelled in terms of superposition of fractional components which may or may not be concerted with the occupancies of the Ln sites. The occupancies of $Ln^{a,b,c,d}(1,2,3,4)$ are: (**7La**) 0.954(6), 0.351(6), 0.898(6), 0.796(6); (**7Ce**) 0.826(3), 0.899(3), 0.834(3), 0.445(3) – in **7La**, site 2 is outstandingly the least populated, but in **7Ce** it is site 4, which would be inversion-related to site 2 in a higher symmetry space group. The assignment of ligand protonation, made on the basis of O···O distances correlates: for **7La**, O(*l*11)···O(*n*21) (*n* = 1, 2) are 2.76(3), 2.81(3) Å, cf. the other O···O distances which range between 3.18(3)–3.34(3) Å; for **7Ce** the shortest distances have become O(*n*31)···O(*n*41) [2.88(1), 3.01(2) Å], cf. 3.07(1), 3.35(1) Å (Table S1, Supporting Information). The depleted sites also correlate in disposition in the unit cell with the depleted sites in the higher symmetry arrays of **5Ln**, **6Ln**.

In both **7La**, **7Ce**, the Ln(1) and Ln(3) sites approach nine-coordination: a pair of LH S(O-μ)$_2$ *fac*-tripod units, the core oxo-atom, an O_2NO bidentate nitrate group, and an ordered pyridine nitrogen atom, assigned a weighting of 0.5. The Ln(2) site is eight-coordinate: a pair of LH S(O-μ)$_2$ *fac*-tripod units and the core oxo-atom making up seven of the sites. In **7La**, the eighth site is occupied by a pair of equally populated fragments of a disordered methanol molecule [O···O 3.37(9) Å], but in **7Ce**, the sites are occupied by components of an *O*-dmso molecule; it may be surmised that of the pair of sites in each case, one of the ligand components corresponds to coordination to an occupancy by Ln, one not. The Ln(4) site also approaches nine-coordination: a pair of LH S(O-μ)$_2$ *fac*-tripod units and the core oxo-atom, comprising seven of the sites. An eighth site in **7La** is occupied by a fully weighted *O*-dmso ligand, the ninth site being occupied 50:50 by *O*-dmso and pyridine ligands, whereas in **7Ce**, both sites are occupied by half-weighted methanol ligands. Half-weighted pyridine residues in the lattice are assigned as components of pyridinium (a) on the basis of charge balance, (b) their proximity, at reasonable hydrogen-bonding distances, one component in each case to coordinated nitrate oxygen [**7La**: N(201)···O(101) 3.04(8); **7Ce**: N(401)···O(301) 3.19(3) Å], and the



(a) (b)

Figure 7. (a) Projection of the complex molecule of $(pyH)_{(2|2)}[O\{Ce(1)(O_2NO)(py)_{0.5}\}\{Ce(2)$(*O*-dmso)$(py)\}\{Ce(3)(O_2NO)(py)_{0.5}\}$-$\{Ce(4)$(*O*-dmso)$_{(2|2)}(py)\}\{(HL \cdot MeCN)_2](\cdot 2H_2O)$ (**7Ce**) [Ce(4) omitted; see text]. (b) Unit cell contents, projected down *b* (*Pn* symmetry).

other to a residue assigned as a half-weighted water molecule oxygen atom [**7La**: N(501)···O(05w) 3.54(11); **7Ce**: N(501)···O(2w′) 2.86(6) Å].

Pr$_3$O(NO$_3$)(LH)$_2$·16H$_2$O·5py·2MeCN ≡ [O{Pr^a(ONO$_2$)(py)$_{(0.67|0.33)}$}{Pr^b(OH$_2$) (py)$_{(0.5|0.5)}$} {Pr^c(*O*-dmso)(py)$_{(0.33|0.67)}$}(HL·MeCN)$_2$]·(3+24/2)H$_2$O·2py (8)

Although of a different crystallographic form, this is the only trinuclear pyridine-containing complex with a fully ordered Ln complement, seemingly capable of providing a useful "baseline" for comparison with **5–7Ln**. One formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure, incorporating a diverse "cocktail" of solvent molecules. The fourth/"empty" lanthanide site, as with the depleted sites of **7Ln** corresponds to the short O···O distances of the ligands [O(131)···O(141), O(231)···O(241) 3.03(3), 2.78(3) Å cf. the other distances which lie in the range 3.15(3)–3.51(3) Å (Table S1)]. Despite the nicely ordered OPr$_3$(HL·MeCN)$_2$ array, Figure 8, the remainder of the structure is no more orderly than those of **5–7Ln** (Table S10, Supporting Information). At Pr^a = Pr(1), a well-ordered nitrate group bonds as a unidentate ligand, but an associated pyridine ligand is modelled as distributed over a pair of sites (0.67:0.33) [N···N′ 0.61(8) Å]. At Pr^b = Pr(2), the coordinated water molecule is well defined, but again the associated pyridine ligand is distributed over a pair of sites (0.5:0.5) [N···N 0.23(5) Å]. At Pr^c = Pr(3), a nicely ordered *O*-dmso ligand is coordinated, but again we find an associated pyridine ligand distributed over a pair of sites (0.33:0.67) [N···N′ 0.25(7) Å]; the possibility of the disorder in the pyridine components being concerted is unclear. Difference map residues in the bulk of the lattice, assigned as water molecule oxygen components, are, in the main, assigned occupancies of 0.5 (no associated hydrogen atoms located). Among them are two fully ordered, fully weighted pyridine components. These interact with the hydrogen atoms of the water molecule coordinated to Pr(2) (O(01)···N(401,501) 2.76(3), 2.84(3) Å. Pr(1) is ten-coordinate: a pair of LH^{3-} OS(O-μ) *fac*-tripod units, the central oxo-atom, a bidentate O$_2$NO nitrate group, and the disordered pyridine. Pr(2) is nine-coordinate: a pair of LH^{3-} S(O-μ)$_2$ *fac*-tripod units, the central oxo-atom, the water molecule oxygen atom, and the disordered pyridine. Pr(3) is also nine-coordinate: a pair of LH^{3-} OS(O-μ) *fac*-tripod units, the central oxo-atom, the *O*-dmso oxygen atom, and the disordered pyridine.

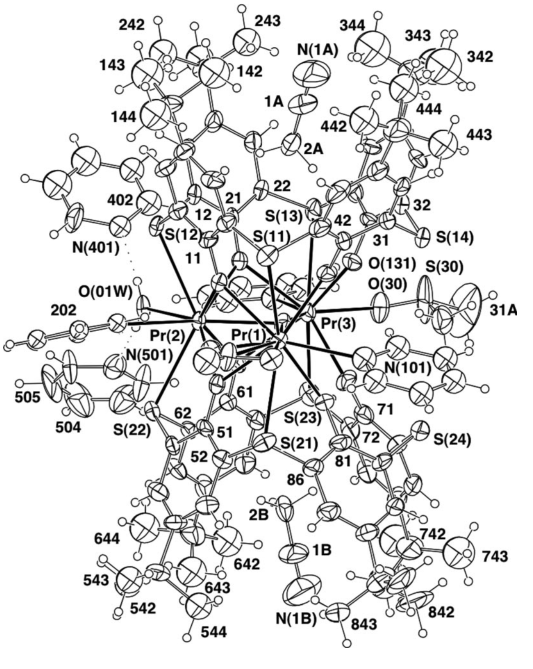


Figure 8. Projection of the complex molecule of [O{Pr(1)(O$_2$NO)(py)$_{(2|2)}$}{Pr(2)(OH$_2$)(py)$_{(2|2)}$}{Pr(3)(*O*-dmso)(py)$_{(2|2)}$}(HL·MeCN)$_2$](·0.25H$_2$O·2py) (**8**), showing the interaction of the two lattice pyridine molecules [N(401),N(501)] with the hydrogen atoms of the coordinated water molecule. O(0)–Pr(1–3) are 2.42(2)(×2), 2.43(2); Pr–O(unidentate) 2.49(2)–2.81(2); Pr–N 2.65(4)–2.84(6) Å. Within the S(μ-O)$_2$ tripods about Pr(2), Pr–S are 3.023(6), 3.032(6); Pr–O 2.45(2)–2.47(2); within the OS(O-μ) tripods about Pr(1,3), Pr–S are 3.072(7)–3.131(7); Pr–O(μ) 2.52(2)–2.54(2); Pr–(other)O 2.35(2)–2.53(2) Å. Pr(2)···Pr(1,3) are 3.687(2), 3.677(2) Å.

Eu$_4$O(OH)$_2$(L)(LH$_2$)$_2$(LH$_4$)·12dmf ≡ [*O*(H*O*)$_2${Eu(*O*-dmf)}$_4$(L·dmf)(H$_2$L·dmf)$_2$](H$_4$L·dmf)(·4dmf) (9)

The core of this complex, postulated as a neutral molecule in the presence of a presumably neutral uncoordinated macrocycle, is an Eu$_4$ core, obligate planar by virtue of its location about a crystallographic mirror plane which lies between the four Eu atoms of the quasi-square Eu$_4$ array (Figure 9; Table S11) and normal to the Eu$_4$ plane, bisecting one of the coordinated ligands. The uncoordinated macrocycle also lies normal to the mirror plane, one-half of the formula unit comprising the asymmetric unit of the structure. An oxygen atom, assigned as "oxo", lies at the centre of the Eu$_4$ plane [deviation 0.019(9) Å]; a further pair of oxygen atoms O(1,2) assigned as "hydroxo" lie in the mirror plane, and to the same side of the Eu$_4$ plane bridging Eu(1) and Eu(2) to their mirror images. Each europium atom is modelled as coordinated in-plane by an *O*-dmf, disordered beyond the oxygen but lying close to the mirror plane and their images. The array is approached by a pair of symmetry-related macrocycles, assigned as (LH$_2$), the bulk of which lie to the same side of the Eu$_4$ plane as the hydroxy groups.

O(111) bridge Eu(1,2) with O(121), S(12) and O(141), S(11) making up OS(O-μ) tripods to either side, coordinating Eu(1) and Eu(2) *fac*, O(121,141) lying 0.047(6), 0.024(6) Å out of the Eu$_4$ plane, just to the side opposite the hydroxy groups. The third macrocycle ('2') is bisected by the mirror plane which passes through O(221,241) and bisects the associated aromatic rings; these two atoms bridge Eu(*l*) and their mirror images, as quasi-reflections in the Eu$_4$ plane of the hydroxo groups. The other phenoxy-*O* donors, O(111,111′) bridge Eu(1)···Eu(2) and their mirrored pair, so that this macrocycle lies "below" the Eu$_4$ plane, i.e. to the opposite side to the hydroxo groups, all four phenoxy-*O* bridging the four Eu atoms. This macrocycle is as-

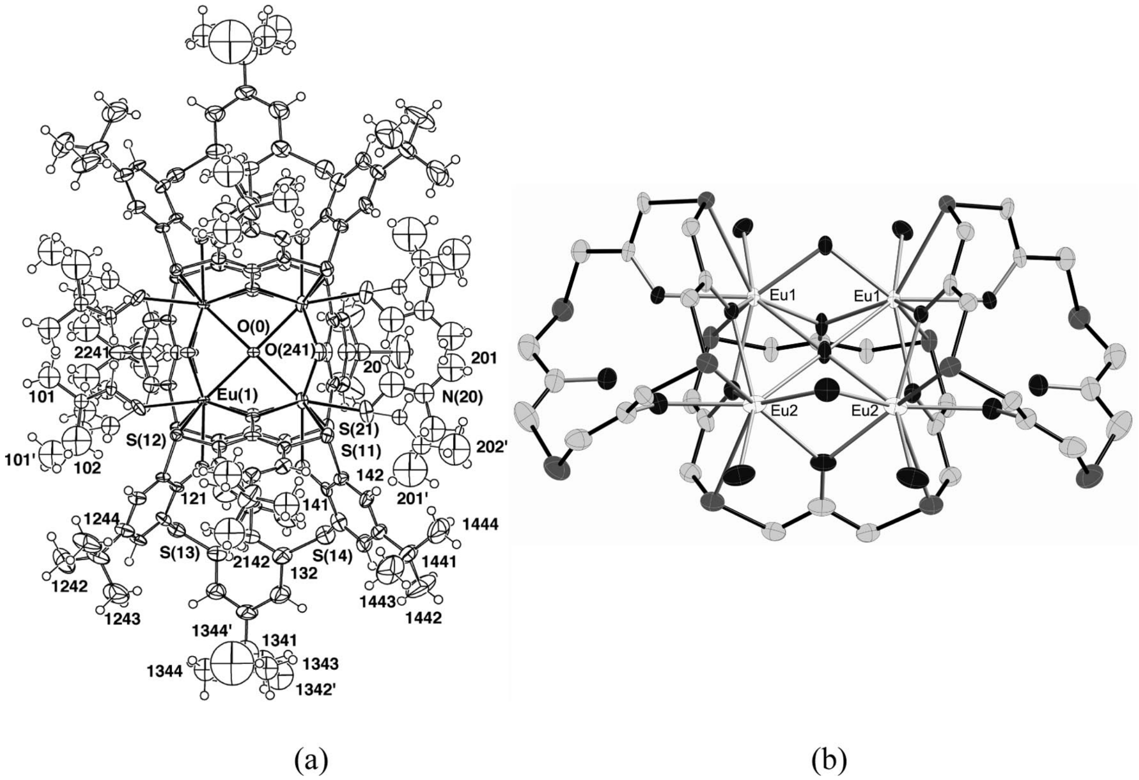


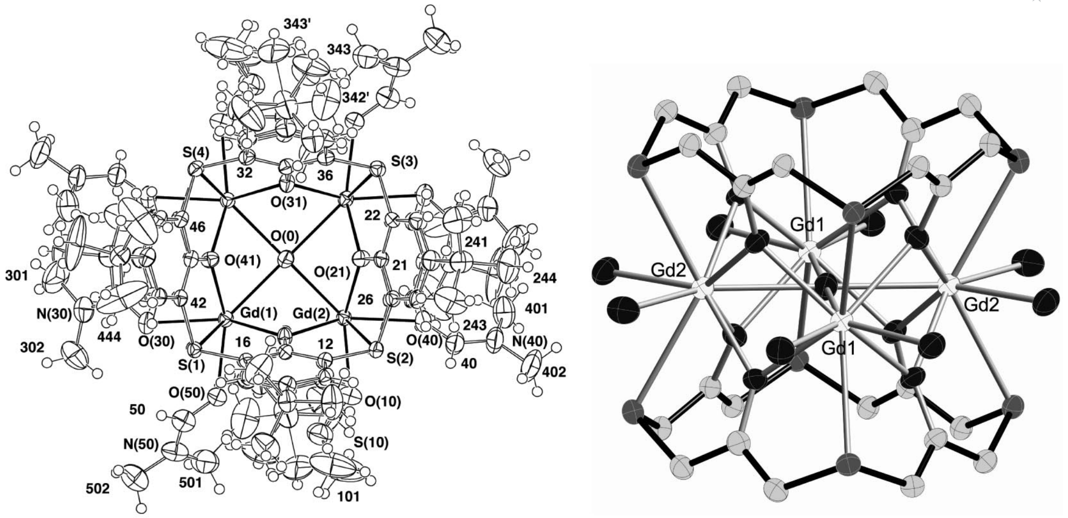
Figure 9. (a) Projection of the complex molecule of $[O(HO)_2\{Eu(O\text{-}dmf)\}_4(L{\cdot}dmf)(H_2L{\cdot}dmf)_2](H_4L{\cdot}dmf)({\cdot}4dmf)$ (**9**) normal to the Eu_4 plane (without included dmf). O(0)–Eu(1,2) are 2.559(6), 2.523(6); O(*l*)–Eu(*l*) are 2.298(5), 2.292(6); Eu–O(dmf) are 2.427(6), 2.413(6) Å. Within the OS(O-μ) tripods, Eu–S are 2.971(2)–3.006(2), Eu–O(μ) 2.407(6)–2.419(5), Eu–O(non-μ) 2.382(5)–2.445(6); Eu···Eu are 3.545(1)–3.631(1) Å. (b) Simplified, perspective view of the coordination core of the complex.

signed as fully deprotonated, in contrast to macrocycle 1, assigned as doubly deprotonated. A third macrocycle, assigned as fully protonated, simply "solvates" the structure, also being bisected by the mirror plane. All macrocycles contain included, disordered dmf. Although the O_4 array of macrocycle 1 is closely planar, the S_4 array is considerably distorted, a distortion reflected in the inclinations of the aromatic rings (Table S1).

Viewed down *c*, the presence of the "free" ligand in the lattice is initially difficult to discern because the molecules project exactly onto positions where the second ligand in a sandwich species would be expected to appear. In fact, the free ligands lie between complex units in such a way that each ligand may be considered surrounded by eight complex units and each complex unit by eight free ligands. Since all thiacalixarene entities adopt a *cone* conformation and all have an included molecule of dmf, these mutual 8:8 arrays have effectively *m*-symmetry. The Eu_4 squares may be regarded as lying in planes parallel to *bc* (so that the perpendicular to the plane, effectively a fourfold axis for the octadentate calixarene ligand, is parallel to *a*), with the free ligand molecules lying in intervening planes. Whereas the free ligands within such planes alternate in orientation within the plane, their effective fourfold axes also being close to oriented along *a*, the complex units have the same orientation in one plane but may be considered rotated by 180° in the next. This results in the dmf-filled octadentate calixarene cavity of one confronting the dmf-filled gap between the two quinquedentate calixarenes of another in the next plane. All the complicated juxtapositioning of these lattice moieties appears to be mediated by dmf molecules via $CH_3{\cdots}O$, $CH_3{\cdots}C$(aromatic) and $CO{\cdots}C$(aromatic) contacts in the range 3.6–3.8 Å, any direct contacts between calixarene units being limited to $CH_3{\cdots}CH_3$ approaches of ca. 3.8 Å or longer.

$Ln_4(OH)(NO_3)_3(L)_2{\cdot}8dmf{\cdot}2dmso{\cdot}3H_2O \equiv [(HO)\{Ln(O\text{-}dmso)(O\text{-}dmf)\}_2\{Ln(O\text{-}dmf)_2\}(L{\cdot}dmf)_2](NO_3)_3({\cdot}3H_2O{\cdot}2dmf)$ (Ln = Pr, Sm, Gd) (10Ln)

Here again, in an array now clearly cationic, defined previously only for Ln = Nd,[5] the core of the complex species is an obligate planar Ln_4 array, effectively square and disposed about a now exactly coplanar central oxygen, by virtue of the disposition of the latter on a crystallographic centre of symmetry, so that one half of the formula unit comprises the asymmetric unit of the structure. The ligand disposition is that of ligand 2 in the preceding complex **9**, disposed completely to one side of the Ln_4 plane, with the four phenoxy-*O* oxygen atoms bridging the four Ln atoms symmetrically; a second symmetry-related ligand lies to the other side of the Ln_4 plane (Figure 10; Table S12), so that the complete array is now a sandwich of the Ln_4O grouping



(a) (b)

Figure 10. (a) Projection of the complex cation of [(HO){Ln(*O*-dmso)(*O*-dmf)}$_2${Ln(*O*-dmf)$_2$}(L·dmf)$_2$](NO$_3$)$_3$(·3H$_2$O·2dmf) (**10Gd**) (as representative of **10Ln**) normal to the Gd$_4$ plane (without included dmf). O(0)–Gd(1,2) are 2.5185(3), 2.5870(3); Gd–O(dmso,dmf) are 2.382(3)–2.420(3) Å. Within the S(μ-O)$_2$ tripods, Gd–S are 2.922(1)–2.976(1); Gd–O(μ) are 2.370(3)–2.397(3), Gd···Gd are 3.6006(4), 3.6204(4) Å. (b) Simplified, perspective view of the coordination core of the complex.

between two macrocycles, differing from the array of **9**, where additional hydroxy groups and an additional macrocycle make up the array. As before, the Ln$_4$O array is extended in the plane by the further coordination of pairs of unidentate ligands, in this case all solvent molecules, (*O*-dmso)(*O*-dmf) about Ln(1), (*O*-dmf)$_2$ about Ln(2); the macrocycle carries included dmf. In view of the coordination mode of the macrocycles, they are assigned as fully deprotonated [all O···O distances (Table S1) are above 3.2 Å], leaving the question of charge balance, as usual, as vexed. The planarity of the Ln$_4$O array renders us loath to assign the oxygen residue as OH (although there are better-authenticated examples in non-calixarene complexes[19]), the only alternative being that the nitrate anions or solvent water molecules may comprise a protonated aggregate or that the proton is bound between the ligands. The disorder found among these residues does not assist the dialogue and we leave the question open, noting the proximity of O(01) to O(101) of nitrate 1 (ca. 2.8 Å) and the fragmentary O(02) to O(20) of the included dmf. The Ln$_4$ unit is very close to an exact square, all four Ln atoms being nine-coordinate in O$_7$S$_2$ environments which contain a pair of S(O-μ)$_2$ tripods. The nitrate anions are not coordinated and, while this may be because they are displaced by dmso, the argument given previously to rationalise the presence of an hydroxo rather than an oxo-group in the trinuclear **5Ln** complexes becomes dubious. The positioning of nitrate outside the metal coordination sphere is associated with short contacts to several other components of the system – O···HC involving *tert*-butyl CH$_3$ (≈ 3.6 Å), dmf-NCH$_3$ (≈ 3.3 Å), aromatic-C (≈ 3.5 Å), S of coordinated dmso (≈ 3.3 Å) and OH$_2$ (ca. 2.8 Å), generally shorter than contacts to "uncoordinated" perchlorate ions of the tetranuclear **11Ln** complexes. This plethora of alternative interactions may explain why here they are not directly bound to Ln.

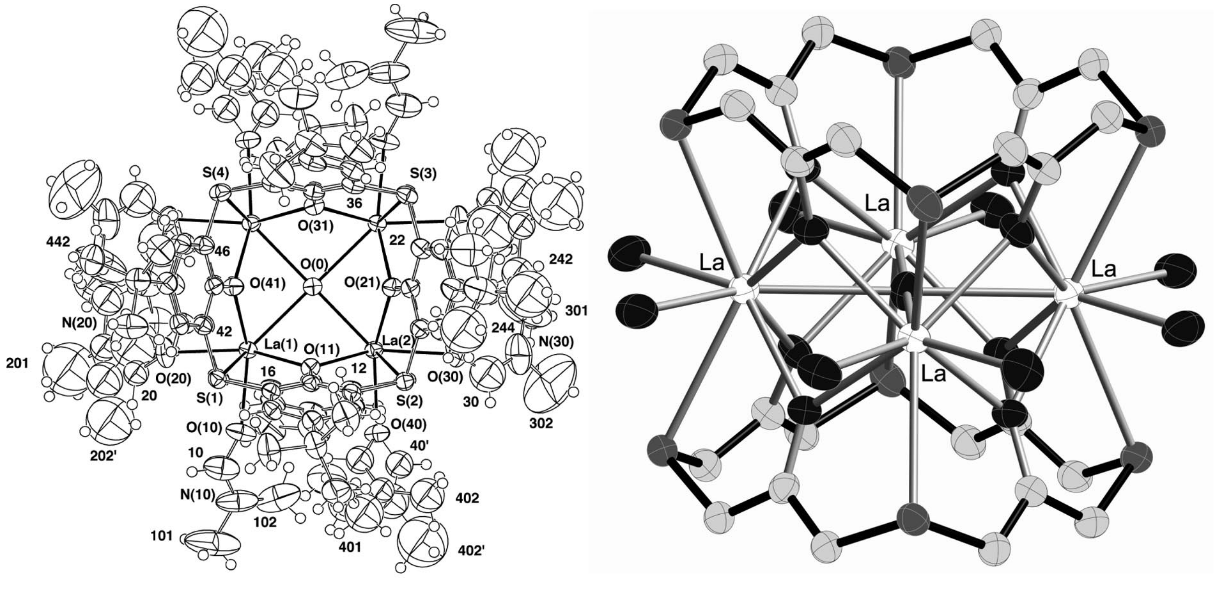
The water molecules hydrogen-bond amongst themselves (O···O ca. 3.0 Å), to the oxygen of coordinated dmso (O···O ca. 3.0 Å) and to the protruding oxygen of included dmf (O···O ca. 2.9 Å). The retention of coordinated dmso from the reactant despite the presence of a much greater amount of dmf in the reaction medium may be associated with attractive interactions between dmso-*S* and adjacent coordinated oxygen atoms:[20] S···O(phenoxide bridge) ca. 3.45 Å, S···O(dmf, coordinated to adjacent Ln) ca. 3.3 Å, although adjacent coordinated dmf molecules also show relatively short O···C(carbonyl) contacts[20,21] of 3.3 Å. Further, the nitrate ions are uncoordinated for crystals obtained here from relatively concentrated preparative media but are coordinated (while, significantly, dmso is not) in the La$_3$O species obtained from a solution approximately three times more dilute, results which would seem anomalous unless simply due to differences in dmso concentration.

Ln$_4$O(ClO$_4$)$_2$(L)$_2$·*x*dmf·*y*H$_2$O ≡ [O{Ln(*O*-dmf)$_2$}$_4$(L·dmf)$_2$]-(ClO$_4$)$_2$[·(*x* – 10)dmf·*y*H$_2$O] (Ln = La, Nd) (11Ln)

Unsurprisingly, given the feebler donor capacity of perchlorate cf. nitrate, the present array is similar in its major components to that of **10Ln**, comprising a sandwich of the OLn$_4$ array between a pair of ligands with quasi-4*mm* symmetry, and again cationic, the anions coordinating in neither. In the present array, moreover, the anion is one which is more prone to disorder, so much so that in the present situation, in the Ln = Nd complex, one of the anions (if indeed present at all) is insusceptible of proper definition, although the complement of **10La** at least avoids the embarrassment in the cation of description in terms of OH rather than O in a square-planar environment. The cation of the present array (Figure 11), otherwise, is also simpler and more satisfying with a homogeneous array of unidentate ligands, all *O*-dmf, all bound, two to each lanthanide, in the equatorial plane of the cation. As in **10Ln**, all metal atoms, drawn from the lighter rare earths, are nine-coordinate (Table S13, Supporting Information). The macrocycle cavities are occupied by dmf. As in **10Ln**, the cation aggregate is disposed with its central oxygen atom on a crystallographic inversion centre, now in space group $P2_1/n$, one-half of the formula unit here also comprising the asymmetric unit of the structure. Although no Ln = La complex was achieved in the **10Ln** array, the coordination environments in **11La** are similar to those in **11Nd** and **10Ln**.

In the lattice of **11Ln**, water and unincluded dmf molecules and perchlorate anions lie in channels parallel to *a* and form partial sheaths about the complex units, so that there are no truly close approaches of calixarene units other than $CH_3 \cdots CH_3$ separations ca. 3.8 Å. The protruding oxygen atom of included dmf seemingly has a short contact to carbonyl-*C* of unincluded dmf and the otherwise quite isolated perchlorate ions appear to make only CH···O contacts with calixarene CH_3 groups. The water molecules associate with unincluded dmf, though disorder makes any detailed analysis of these and other presumably weak lattice interactions impossible. That perchlorate anion is not within the primary coordination sphere of the lanthanide is perhaps unsurprising, though perchlorate certainly can ligate La^{III} and there are even reasons for expecting a ligand capable of forming four-membered chelate rings to be relatively effective at doing so with very heavy metals.[22]

The lanthanide atoms are nine-coordinate, four phenoxide-*O* and two thiaether-*S* [from two $S(O\text{-}\mu)_2$ *fac*-tripods (Table S13)], forming an approximate trigonal prism, with two dmf-*O* and the central oxide being face-capping. The planar Ln_4O unit is symmetrically sandwiched between two calixarene units (Figure 11) which have regular *cone* conformations, each including a molecule of dmf, the latter, along with the unidentate ligands in the plane of the metal atoms, degrading the idealised symmetry of the cluster. This sandwich structure, in which the calixarene ligands are octadentate, has now been seen with a remarkable range of metal ions, with the M_4-square side varying from ca. 3.0 Å (Cu) to 3.76 Å (La), while M–O(L) varies from ca. 1.93 (Cu) to 2.5 (Pb)[1] and M–S from 2.4 (Cu)[2,4] to 3.1 (Pb, La) Å (Table 1). The phenyl groups of the calixarene may adopt different tilt angles to the mean S_4 plane in order to achieve these specific separations in spanning the M_4 square, though it would appear that without significant distortion from a regular *cone* conformation, the calixarene requires a difference of ca. 0.6 Å between M–O and M–S. Thus, with Hg^{II},[8] for which <M–O> is 2.39(4) Å and <M–S> is 2.61(1) Å (an even smaller difference than with Pb^{II}), the calixarene is strongly distorted, while the present array is least.



(a) (b)

Figure 11. (a) Projection of the complex cation of $[O\{Ln(O\text{-dmf})_2\}_4(L\cdot dmf)_2](ClO_4)_2[\cdot(x-10)dmf\cdot yH_2O]$ (≡ $13dmf\cdot 2H_2O$) (**11La**) (as representative of **11Ln**) normal to the La_4 plane (without included dmf). O(0)–La(1,2) are 2.6908(3), 2.6238(4); La–O(dmf) are 2.463(4)–2.500(4) Å. Within the $S(\mu\text{-}O)_2$ tripods, La–S are 3.023(1)–3.091(1); La–O(μ) are 2.488(4)–2.524(4), La···La are 3.7531(5), 3.7635(5) Å. (b) Simplified, perspective view of the coordination core of the complex.

Table 1. Comparative $[(O)M_4\{LH_{(x)}\}_2]^{(n\pm)}$ dimensions.

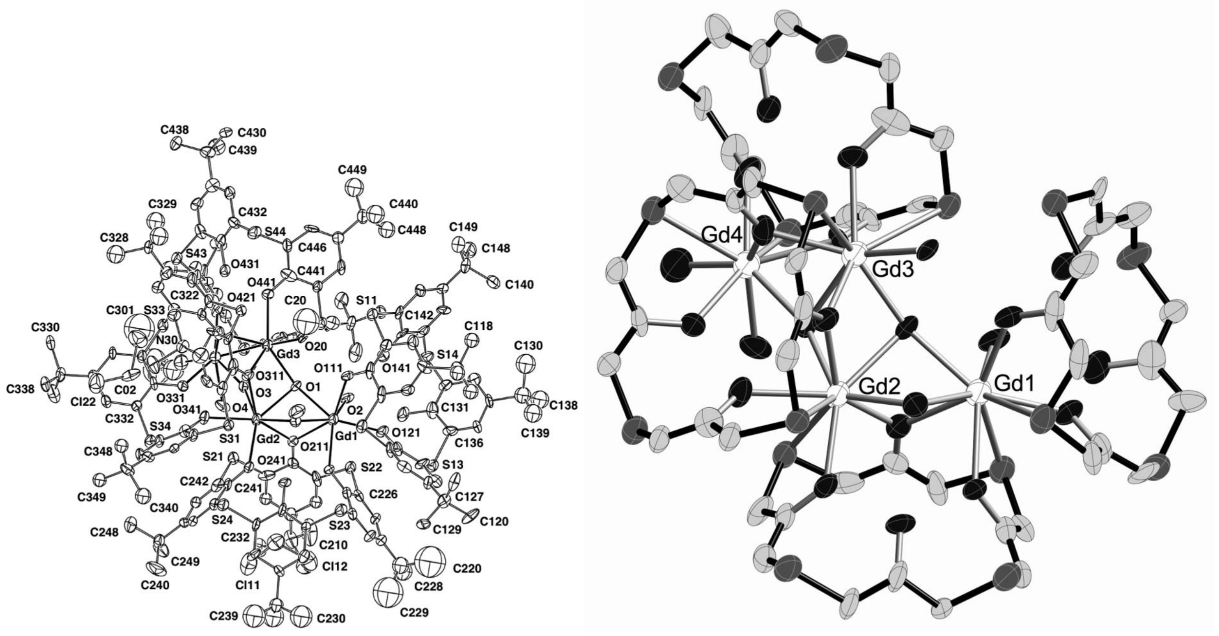
M	Cu(mol. 1)[4]	Cu(mol. 2)	Pb[1]	Hg[8]	**10Gd**	**11La**
Distances [Å]						
M···M	2.970(2) –3.055(2)	2.980(2) –3.048(2)	3.6688(4), 3.6754(5)	3.7344(5) –	3.6006(4), 3.6204(4)	3.7531(5), 3.7635(5)
M–O(central)	–	–	2.4829(3), 2.7055(4)	–	2.5185(3), 2.5870(3)	2.6238(4), 2.6908(3)
M–O(L)	1.929(5) –2.431(5)	1.925(6) –2.389(5)	2.4565(5) –2.563(7)	2.318(7) –2.452(7)	2.371(3) –2.389(3)	2.488(4) –2.512(3)
M–S(L)	2.413(3) –2.891(3)	2.415(3) –2.862(3)	3.111(2) –3.161(2)	2.603(3) 2.620(3)	2.929(1) –2.976(1)	3.023(1) –3.091(1)
Interplanar dihedral angles [C_6(ar)/M_4] [°]						
θ	40.8(2) –71.6(2)	40.7(2) –70.4(2)	44.7(2) –69.9(2)	43.5(3) 88.3(3)	57.8(1) –69.7(1)	60.5(1) –72.0(2)

$Gd_4O_2(LH_2)_4\cdot 2H_2O\cdot 2MeOH\cdot dmf\cdot 3.375CH_2Cl_2 \equiv [Gd_4O_2(LH_2)_2(LH_2\cdot CH_2Cl_2)_2(OH_2)_2(HOMe)_2(O\text{-dmf})](\cdot 1.375CH_2Cl_2)$ (12)

This last tetranuclear array provides a novel form strikingly different to the previous arrays. The molecular core may be viewed as (dmf-*O*)(H_2O)Gd(μ_3-O)Gd(HOMe)(μ_3-O)Gd(μ-HOMe)Gd(OH_2) – a "Z"-shaped array in which the gadolinium atoms are linked by a pair of triply bridging oxo-ligands and a bridging methanol molecule, the dihedral angle between the pair of peripheral Gd_3 planes being 47.26(3)°. One full independent, neutral molecular aggregate, devoid of any crystallographic symmetry, comprises the asymmetric unit of the structure (Figure 12). The environments of the four independent gadolinium atoms (Table S14) are similar in that each is nine-coordinate, comprising a pair of OSO tridentate/*fac*-tripodal calixarene ligands and three other oxygen atoms. In the case of an inner gadolinium atom, all of these may be bridging [Gd(2)], or, at the other extreme, at a peripheral [Gd(4)], only one may be; about all gadolinium atoms the three non-thiacalixarene oxygen atoms form a quasi-planar "*mer*" array about the gadolinium atom. The gadolinium atoms differ, however, in their connectivities, in which the thiacalixarene ligands have diverse roles, all of the latter behaving differently. Two of the ligands have ordered, included dichloromethane molecules (ligands 2,3; CH_2Cl_2 molecules 1,2), further solvent molecules filling voids in the lattice array. With the exception of ligand 1, which interacts with Gd(1) as a simple OSO *fac*-tripod ligand, the interactions of the other three ligands are as bridging entities of diverse forms: ligand 2 behaves as a double *fac*-tripod, OS(O-μ)SO, with the central oxygen atom, O(211), bridging Gd(1,2); the behaviour of ligand 3 is even more complex, as a triple *fac*-tripod OS(O-μ)S(O-μ)SO, with O(311) bridging Gd(2,3), and O(321) bridging Gd(3,4), the environment of Gd(3) containing a pair of bridging ligand oxygen atoms O(311,321); ligand 4 again, like ligand 2, forms a double *fac*-tripod, O(411) being shared between Gd(3,4). The O_4 arrays of ligands 1–3 are appreciably non-planar (Table S1), the distortions diminishing in that order.

Considering the gadolinium atom environments in more detail, the environment of Gd(1) comprises a terminal water molecule ligand, O(2), a μ_3-oxo ligand O(1), a μ_2-methanol ligand oxygen, O(10), and thiacalixarene ligands 1 [through O(111,121); an OSO *fac*-tripod], 2 [through O(211,221); an OS(O-μ) *fac*-tripod], one of the oxygen atoms [O(211)] from the latter bridging to Gd(2). The environment of "inner" Gd(2) comprises the pair of μ_3-oxo ligands, O(1,6), together with the μ_2-oxo methanol [O(10)], and a pair of OS(O-μ) *fac*-tripods derived from thiacalixarene ligands 2 [through O(211,241)] and 3 [through O(311,341)], O(211) and O(311) bridging to Gd(1) and Gd(3) respectively. The environment of the other "inner" Gd(3) comprises the pair of μ_3-oxo ligands O(1,3), a terminally coordinated methanol molecule [O(3)], and a pair of OS(O-μ) *fac*-tripod ligands, derived from thiacalixarene ligands 3 [through O(311,321)] and 4 [through O(411,441)], both of O(311,321) being bridging [to Gd(2,4)], O(411) also bridging to Gd(4). The environment of the other "peripheral" Gd(4) comprises one μ_3-oxo ligand, O(6), and terminal *O*-dmf, [O(30)], and water molecule [O(4)] ligands, together with a pair of thiacalixarene OS(O-μ) *fac*-tripod ligands 3 [through O(321,331)] and 4 [through O(411,421), O(321,411) bridging to Gd(3)].

Although thiacalixarene protonic hydrogen atoms have not been located in difference maps or included in the refinement, charge balance considerations require that, if the μ_3-oxygen atoms are assigned as unprotonated "oxo" species, and water and methanol ligands are assigned as neutral, the eight protonic hydrogen atoms remain to be distributed over the four thiacalixarene ligands, i.e. notionally two per ligand. The unsymmetrical involvement of the latter with the gadolinium atoms, ranging from one tripodal interaction in the case of ligand 1, to three in the case of ligand 3, suggests the possibility of a correspondingly unsymmetrical disposition of protonic hydrogen atoms, e.g. $(L^1H_3)(L^2H_2)(L^3H)(L^4H_2)$ rather than $(LH_2)_4$ as likely. The O···O interdonor distances of Table S1 are somewhat ambiguous, favouring the assignment of six, rather than eight protons, although that could be accommodated by the assignment of hydroxo- rather than oxo- bridges, O(1,3), and the situation is compounded by the possible presence of



(a) (b)

Figure 12. (a) Projection of $[Gd_4O_2(LH_2)_2(LH_2{\cdot}CH_2Cl_2)_2(OH_2)_2(HOMe)_2(O\text{-dmf})]({\cdot}1.375CH_2Cl_2)$ (**12**). O(1)–Gd(1,2,3) 2.453(2), 2.531(2), 2.323(2); O(3)–Gd(2,3,4) 2.391(2), 2.475(2), 2.381(2); Gd(4)–O(4) 2.564(2) Å. O(10)–Gd(1,2) 2.277(2), 2.313(2); O(20)–Gd(3) 2.401(2); O(30)–Gd(4) 2.316(2) Å. [O(1–4) water/oxo group oxygen atoms; O(10,20) methanol; O(30) dmf]. Within the OS(O-μ) tripods: Gd(1)–S(12,22); Gd(4)–S(33,42) 2.983(1), 3.059(1); 2.9223(9), 3.069(1); Gd(1)–O(111,121); Gd(3)–O(311,321) 2.338(2)–2.389(2); Gd(1)–O(221), Gd(4)–O(421) 2.495(2), 2.349(2); Gd(1)–O(211)(μ), Gd(4)–O(411)(μ) 2.508(2), 2.403(2) Å. Gd(2)–S(21,31); Gd(3)–S(32,41) 3.049(1), 2.958(1); 2.942(1), 2.9908(9) Å. Gd(2)–O(241), Gd(3)–O(441) 2.333(2), 2.446(2) Å. Gd(2,3)-(μ-O): Gd(2)–O(211), Gd(3)–O(411) 2.379(2), 2.391(2); Gd(2)–O(211,311), Gd(3)–O(311,321) 2.337(2)–2.389(2) Å. Gd(1)···Gd(2) 3.5627(3); Gd(3)–Gd(2,4) 3.5548(3), 3.5774(3) Å. (b) Simplified, perspective view of the coordination core.

hydrogen-bonding interactions intramolecularly from the methanol ligands O(10,20) (the OH hydrogen atoms may be postulated from difference map evidence and are included in the model), O(10)···O(231) being 3.100(3), O(20)···O(111) 2.726(3) Å. Hydrogen-bonding is also possible between the water molecule O(2) and O(131,141), the associated O···O distances being 2.725(3), 2.778(3) Å.

Summary of Remarks on the Lanthanide Ion Complex Structures

In overview, complexes of the lighter lanthanides proved to be the easier to isolate, though crystallisation still required considerable patience, with long periods of deposition commonly bringing their own problems. In the case of the different complexes obtained from reactions of $[Ln(dmf)_8](ClO_4)_3$ and $[Ln(dmso)_4(NO_3)_3]$, for the "early" Ln, for example, for La, the well-developed crystals deposited from dmf over periods of months at ambient temperature proved, in both cases, to be those of hydrolysis products due to adventitious water. Thus, from the perchlorate reactant, the crystallographically characterised material was the tetranuclear complex postulated as **11Ln**. Unlike the also tetranuclear array in **10Ln** (see below), the atom at the centre of the Ln_4 square appears to be an oxide, rather than hydroxide, anion, though there is evidence that interconversion of Ln_4O and $Ln_4(OH)$ clusters bound to other multidentate ligands can be readily achieved.[19]

The structure of **5Ln** [Figure 5, (a)], the trinuclear hydroxo complex obtained by using $[Ln(dmso)_4(NO_3)_3]$ in place of the $[Ln(dmf)_8](ClO_4)_3$ used to provide the tetranuclear **11Ln** species, shows that nitrate is certainly capable of chelating La^{III} in the presence of the thiacalixarene coligand. Coordination of nitrate would reduce the complex ion charge and hence the acidity of coordinated water and thus its presence might explain the isolation of this complex as a hydroxo- rather than an oxo-species, though this is obviously not the only factor which must be considered. (In addition, because phenolic protons were not located in the structure refinement, it is possible that oxide ligand could be present along with one LH_3^- ligand.) Along with the tetranuclear species discussed above, this trinuclear complex may be considered to typify the chemistry of at least the first half of the lanthanide series with *p*-*tert*-butyltetrathiacalix[4]arene, where a divergent, ditopic receptor is formed by the sandwiching of a small, hydrolytically-produced metal cluster, garlanded by a variety of simple ligands, between two near-regular *cone*-form macrocycles. Despite long-term application to the problem of crystallising a Ce^{IV} complex of a calixarene,[23] the present work yielded only the crystal structure of the Ce^{III} species, **5Ce**, the Ln_3 unit here, as throughout the array, being composed of two ten-coordinate and one nine-coordinate metal centres. Although intense violet colours in solution assumed to be indicative of formation of a Ce^{IV} complex could be observed, the stability of this complex, perhaps because of the availability of reducing thiaether centres, seemed to be even less than that of complexes formed with methylene-bridged calixarenes.

An illustration of the subtlety of the factors influencing lanthanide/thiacalixarene complex crystallisation is provided in the isolation of a tetranuclear hydroxo species containing no directly coordinated nitrate from the reaction between $[Ln(dmso)_4(NO_3)_3]$ and LH_4 in dmf/triethylamine. Green **10Pr** is isomorphous with its violet **10Nd** analogue described in an earlier publication,[5] one of the notable features of the composition of these materials being the presence of three small, neutral molecules, water, dmso and dmf, with the dmf having two roles, being both included by the calixarene and coordinated directly to the metal. In this regard, it should also be noted that in **11La** the dmf has three roles, being located between complex units as well as included and coordinated.

When only perchlorate and dmf are present in place of any nitrate and dmso in the preparative medium, the Nd^{III}/thiacalixarene complex precipitates as the OH-deprotonated derivative of the Nd_4OH species just discussed. The structure of this compound **11Nd** shows a complex unit essentially identical to that in the La^{III} analogue [Figure 11, (a)], again involving nine-coordinate metal centres, though the two crystals are modelled with different solvent compositions. Unfortunately, both are hydrated, so it is not possible to say from infrared spectral measurements that the absorption assigned to the OH group in **10Nd**[5] has disappeared. Consideration of the Nd–O bond lengths in the two compounds [Nd_4OH 2.6329(2) 2.5735(2) (**10Nd**); Nd_4O 2.6385(4), 2.5460(4) Å (**11Nd**)] (both *T* ca. 153 K) leads to no greater certainty as to assigned proton locations.

Just as syntheses of Ln_4O species may be reproducible from at least La–Nd, so, too, appear to be the preparations of trinuclear **5Ln**, in that the La, Ce and Nd species are isomorphous, showing that ten-coordination, at least when it is a consequence of the presence of the small-bite chelate nitrate, can extend at least as far as Nd. Although the Ce complex was not obtained from similarly "dilute" reaction media to those used for La and Nd, it is a special case since the reaction mixture had been designed to obtain the Ce^{IV} species (see above) and dmso was absent. Nonetheless, it must be noted that the crystallisation periods for these (and most other) complexes varied widely, suggesting kinetic factors could influence the form of crystalline material, and further support for this caution is provided in the results obtained in extending the $[Ln(dmso)_4(NO_3)_3]$ in dmf method to Sm^{III}.

Thus, an initial effort to conduct the complexation reaction using $[Sm(dmso)_4(NO_3)_3]$ in "dilute" dmf solution provided (over 1 month) crystals of **10Sm**, isomorphous with the Pr and Nd analogues obtained from "concentrated" solutions. In attempting to repeat this synthesis, crystals deposited within a few days proved to be the binuclear **1**, an interesting species in that it may be an intermediate in the hydrolytic oligomerisation presumably involved in the formation of Ln_3L_2 and Ln_4L_2 species in these reaction systems. The two calixarene ligands have a very similar mutual orientation to that in the complexes of higher nuclearity and their conformations are quite regular *cones*, again as in the other complexes, suggesting that this must be a relaxed arrangement in Ln^{III} systems, at least between La and Sm. Both Sm centres are nine-coordinate, with O_7S_2 environments.

A third Sm^{III} complex, which proved (now, not surprisingly) to be a trinuclear Ln_3L_2 species even though derived from a reaction mixture in which Ln/L was 2:1, has no direct relation to the complexes discussed to this point, since it was the first complex derived from the only method of synthesis discovered to work well for the whole lanthanide series, to be obtained in a form suitable for a structure determination. It provides firstly a striking illustration of the complicated stoichiometry possible for these thiacalixarene complexes. The complex was modelled from the structure determination as **7Sm** (Figure 7), containing four different solvents, acetonitrile, dmso, pyridine and water, with pyridine present both bound and unbound to the metal, and water present not only like this but also in its deprotonated form as an oxide ligand. Acetonitrile is apparently the preferred occupant of the calixarene cavities. Comparison of the Sm–O(xide) distances here [2.4353(4), 2.6307(7) Å] with those for the related bonds in the $Sm_2(OH_2)$ [2.507(7), 2.531(7) Å] and Sm_4OH [2.6028(3), 2.5491(3) Å] species in **1** and **10Sm** does little to provide any structural criterion of the state of protonation of the bridging oxygen. What relationship there may be between the structure determined for the recrystallised material and that of the complex initially precipitated from dmso is unknown, though analyses of the crude products obtained for the full lanthanide series were mostly consistent with the formulation $Ln_3OL(LH)(NO_3)\cdot n$dmso.

Despite the rather heterogeneous nature of the equatorial garland of unidentate ligands bound to the Sm_3 unit in **6Sm**, the sandwich is quite symmetrical, with acetonitrile molecules included in both diametrically opposed, essentially *cone*-form cavities. Disorder of the three Sm atoms involves their distribution over the four metal sites of the Ln_4 sandwich species discussed above. Within the Sm_3 unit, the central Sm is bound to unidentate nitrate and water, while the outer Sm have pyridine and dmso as unidentate ligands, all three, despite these differences, remaining nine-coordinate, with O_7S_2 or O_6NS_2 environments completed by the calixarene donors.

In the four isolated complexes of Eu^{III}, all continue to involve nine-coordination of the metal (mostly O_7S_2 environments) but three (**3**, **4**, **9**) have unique structures not yet observed with any other Ln^{III}. The fourth provides another example of the complicated stoichiometry possible referred to above, as the complex is of the **6Ln** form, though in fact the other complexes have structures which make this appear quite a simple species! An unusual feature of the lattices in two of the three unique complexes is the presence of uncoordinated calixarene molecules (and at least one other example of an Eu^{III}/calixarene complex having this nature is known[24]). Eu^{III}, as the most readily reduced lanthanide(III) ion, forms complexes with calixarenes which are generally coloured yellow as a result of an LMCT absorption near 400 nm,[23] and in this sense they are unique in the series. If there is significant electronic modification of the ligand in the primary coordination sphere as a result of such interaction, this may promote more distant interaction with another ligand. While the two present structures do show intimate contact between "free" and coordinated ligands, they do not, however, provide evidence for any otherwise unusual mode of contact between them.

The tetranuclear complex **9** is novel in that although it contains an essentially square-planar OLn_4 entity as seen in several instances described above and elsewhere,[5] this is not held within a sandwich defined by two opposed calixarene ligands. Of course, since it was obtained in very low yield and it is possible that some unrecognised variation in procedure led to its crystallisation, its novelty may not be of any particular significance in respect of abundance in solution, but its structure can nonetheless be taken to indicate one possible form. The structure determination resolves an issue not uncommonly encountered in lanthanide chemistry[25] where the stoichiometric metal/ligand ratio (here 1:1) is not indicative of the actual ratio in the complex species present. The complex unit [Figure 9, (a)] has Eu/L 4:3 and the bridging of two opposite edges of the Eu_4 "square" (Table S15, Supporting Information) by hydroxo ligands, both to the same side of the face of the square, presumably explains why a single calixarene does not lie above this face, though a single octacoordinate species lies above the other, and why instead two quinquedentate (O_3S_2) calixarene entities bridge the edges lacking hydroxide, though why the hydroxo ligands appear in this particular case is obscure.

Certain aspects of the structure of trinuclear **3** involve reproduction of a familiar situation in that the complex unit [Figure 3, (a)] contains an Ln_3O entity held in a true sandwich of two calixarene ligands, each calixarene having a close-to-regular *cone* conformation, with occupancy of the cavities by dmf suggesting that the complex might be used as a divergent, ditopic receptor. Presumably in consequence of the presence of this sandwich form, the extra mol of ligand responsible for the Eu/L stoichiometry being 3:3 is incorporated into the lattice in a quite different way to that observed in the tetranuclear complex, **7**, discussed above. **6Eu** may be a member of a form of complexes (**5Ln**, **6Ln**) similar for all lanthanides, and, although three of the four Eu^{III} complexes considered here do contain a sandwich species similar to those found for all other early lanthanides, overall numerous features indicate that there may be something unique about the interaction of Eu^{III} with *p-tert*-butyltetrathiacalix[4]arene.

Other evidence that Eu^{III} provides a special case is apparent in the reproducibility of the "concentrated solution" synthesis for the following element, Gd, where **10Gd**, isomorphous with its Pr, Nd and Sm analogues, is obtained. This product, all the same, was obtained only after a long period of standing of the reaction mixture in ambience and it is still unclear what the period required is for hydrolysed species to be formed in solution or what relations exist between the precipitated species and the major forms in solution. The effect of the lanthanide contraction is that species change can occur as the Ln series is traversed and the change in, for example, the Ln_4 unit edge-length between Pr and Gd in this particular isotypic group of Ln_4OH complexes is a quite substantial ca. 0.1 Å, so that if the solid phases are in some way indicative of what is in solution, then it appears that significant changes may occur between Gd and Yb in respect of the species encountered. This is reflected in the crystallisation, from a "dilute" medium in the case of Yb^{III} and a "concentrated" medium in the case of Lu^{III}, of very similar trinuclear species which, although they involve two calixarene ligands, do not have a true sandwich structure. In fact, as is apparent from the form of the trinuclear **2Ln**, [Figure 2, (a)], there is some resemblance to the Ga^{III} and V^{V} complexes[2] rather than to the earlier Ln^{III} complexes. The hydroxo-bridged metal oligomer at the core of the complexes is, however, more complicated than in those of the transition metal derivatives, being an $Ln_3(\mu_3\text{-}OH)_2(\mu\text{-}OH)$ unit in which the μ_3-OH ligand oxygen atoms lie disposed slightly unsymmetrically above and below the centroid of the Ln_3 triangle [δO(*n*1,2) 1.19(2), –1.26(2) (mol.1); 1.16(2), –1.21(1) (mol.2)(Yb); 1.17(1), –1.21(1); 1.16(1), –1.21(1) Å (Lu)] while the μ-OH oxygen lies outside one edge and slightly toward the O(*n*2) side of the plane [0.21(2), 0.16(1) (Yb); 0.20(1), 0.14(1) Å (Lu)]. The other two edges of the triangle are spanned by quinquedentate (O_3S_2) calixarene ligands and the two Yb atoms linked by the μ-OH group each have one dmf and one aqua ligand, so that all three Yb are eight-coordinate but the central Yb has an O_6S_2 environment while the outer two have O_7S. The chiral complex has close to C_2 symmetry. The calixarene ligands remain conical and each includes a molecule of dmf, so clearly there is the potential for the Yb and Lu complexes to behave as twisted ditopic receptors.

That a species change occurs across the Ln series appears only to be established for crystals obtained from dmf medium containing the lanthanide nitrates, as the Sm, Eu, Dy and Lu complexes, **6Ln**, obtained by initial reaction in dmso followed by recrystallisation from pyridine/acetonitrile (by presumption, Sm through Lu, including Y) are isomorphous, though of course it may be that the failure to obtain suitable crystals with Ln lighter than Sm is a consequence of a change early on. This Lu complex does have a sandwich form, presumably at least in part because there is only a single oxo-ligand at the centre of the Lu_3 cluster. There is also a return to nine-coordination of the metal. Since the acidity of $Ln–OH_2$ increases across the Ln series,[26] the association of Lu_3 with three $OH^–$ in the complex obtained from dmf solvent can be considered unsurprising and perhaps the common structure of the Sm, Eu, Dy and Lu complexes obtained from pyridine/acetonitrile after synthesis in dmso reflects simply a more limited availability of adventitious water in this system. At present, it would seem that the presence of an hydroxo- or oxo-bridge linking all metal atoms is essential to the crystallisation of polynuclear lanthanide complexes of *p-tert*-butyltetrathiacalix[4]arene so that the complete exclusion of water might lead to quite different chemistry.

Conclusions

Although ambitions to complete a Periodic Table of thiacalixarene complexes have not been fully realised in the present trilogy of studies, it has shown *p-tert*-butyltetrathiacalixarene to be a ligand of considerable versatility and one of particular utility in converting small clusters of metal ions into lipophilic entities.[10] Not reported here is a large number of investigations of syntheses that did not lead to crystalline complexes suitable for structure determinations, and there is certainly a vast amount of solution chemistry that remains to be characterised. The case of Cr^{III} complexes illustrates both some of the intriguing aspects and the frustrations of this work. As expected for an inert metal ion, formation of Cr^{III}/thiacalixarene complexes required quite extreme conditions, giving products with properties very dependent on the reaction time. Reaction of the solution obtained by dissolving $CrCl_3\cdot 6H_2O$ in dmf (and distilling the mixture to remove water[27]) with thiacalixarene/triethylamine gave dmf-soluble green material after 5 min at the boiling point. This could not be crystallised on cooling the mixture, though partitioning between water and toluene produced some insoluble material and a green toluene extract. Concentration of this extract gave an amorphous residue that could be dissolved in acetone but then slowly deposited an amorphous green powder. After 15 min initial reaction time, the material obtained by partitioning was no longer soluble in acetone but partly soluble in hexane and, after 30 min reaction, the product seemed entirely soluble in hexane. Again, however, concentration of a hexane solution led only to the deposition of an amorphous green powder. This hexane solubility represents an extreme of lipophilicity for the complexes presently studied but indicates the potential of the thiacalixarene for introducing possibly catalytically active metal clusters[28] into apolar media.

One of the striking characteristics of *p-tert*-butyltetrathiacalix[4]arene as a ligand[9] is that it retains a conformation that can be described as conical in all but one[29] of its complexes known to date, even if there are considerable distortions from a *cone* of true fourfold symmetry. This is not always the case for complexes of various derivatives of the calixarene[11,30–33] except the thiacalix[4]aniline,[33] though investigations of the structural coordination chemistry of this last ligand are, so far, limited. Inclusion of molecules such as dmf, CH_2Cl_2, MeCN, $CHCl_3$, MeOH, Me_2SO, pyridine and thf,[1–3,9,16a,17] as well as hermaphrodite pair formation,[3] appear to require that the calixarene adopts close to a regular *cone* conformation, though systematic efforts to exploit distorted conformations seen in various metal complexes are yet to be made. It is worth noting, however, that the two nearly parallel phenyl rings of calixarene units found in the W^{VI} and Hg^{II} complexes[2,8] do not have the cocrystallised solvents (benzene for W and mesitylene for Hg) inserted between them. This may mean here that edge-to-face aromatic interactions are preferred to stacking arrangements,[34] or, given that inclusion is the result of weak interactions, perhaps not just involving the cavity,[18] that four points of interaction are required to favour inclusion over other possibilities. (A similar argument has been used to rationalise the different behaviour of Cs^{I} towards *p-tert*-butylcalix[4]arene and *p-tert*-butyltetrathiacalix[4]arene monoanions.[3]) While this is an issue requiring further exploration, even just the currently known thiacalixarene complex systems with close-to-regular *cone* conformations offer a wide variety of "molecular connectors", if their inclusion abilities can be exploited without other modification of the complex structure (a point that is not certain, given that most metals involved are labile). Thus, the tetranuclear Ba^{II}[1] and dotricosa-Ni^{II}[2] complexes offer octahedral connectors of rather different dimensions, the tetranuclear In^{III} complex[1] offers a tetrahedral connector, the tetranuclear Eu^{III} complex (present work) a trigonal connector, and numerous systems offer bent, twisted and linear ditopic connectors. How useful it may be to have such potential tectons for solid-state materials design is an important question, but bifunctional "plugs" such as viologen dications,[35] for example, might allow electronic interactions between polymetal units held by the calixarenes and so produce new, highly anisotropic crystals.

The maximum denticity towards metal ions exhibited by the thiacalixarene is eight, involving its four *O*- and four *S*-donors, and is observed in several lanthanide, transition metal and at least one main group metal (Pb) complexes. Presumably the appropriate choice of metal ion would allow this to be increased by use of the phenyl rings as donors.[10,18,36] Restrictions of the spatial array of the sulfur and oxygen donors, which result from the macrocyclic structure of the ligand, may explain the efficiency with which octadenticity is achieved with a planar, essentially square tetrametal unit, though the conformational flexibility of the calixarene is still sufficient for it to adapt to M_4 arrays of significantly different dimensions.[37] Binding to an M_4 unit need not be associated with sandwich complex formation, as seen in the cases of Cu^{II},[2] Eu^{III} and a known Zn^{II} species,[38] and this is perhaps an area of thiacalixarene chemistry which warrants further attention in that the macrocycle could simply act as a scaffold to hold an accessible multimetal reaction centre together. This, of course, would also apply to the range of substituted thiacalixarenes,[9] which have already been shown to have their own remarkable coordination chemistry.[11]

In terms of the basic coordination chemistry of *p-tert*-butyltetrathiacalix[4]arene, an issue neglected by the present work is the possible nature of complexes formed under truly anhydrous conditions. Many complexes of (methylene-bridged) *p-tert*-butylcalix[4]arene prepared in this fashion have been shown to generate important new chemistry.[39] The unsophisticated methods of synthesis utilised in the present work have resulted in the common isolation of complexes that can be regarded as metal-aqua complex hydrolysis products, and it is unclear how important this may be in determining their structure, though M_4 complexes, for example, can be obtained with and without a central oxo or hydroxo ligand. Calixarene anions are aryloxides and many stark contrasts in the behaviour of aryloxides and oxo/hydroxo-aryloxides are well known.[40] Ultimately, both areas may need to be thoroughly explored to gain a full understanding of the solution coordination chemistry of thiacalixarenes, although there are certainly areas where substantial progress has already been made.

Experimental Section

Synthesis and Crystallisation: In the process of searching (unsuccessfully) for a common method of synthesis and crystallisation which would enable the structural characterisation of the complete rare earth (including Y) series as thiacalixarene complexes, a variety of synthetic procedures involving a range of metal/ligand ratios were explored. The nearest approach to a synthesis suitable for the full lanthanide series was found to be that based upon an initial reaction in dmso followed by recrystallisation from pyridine by addition of methanol and/or acetonitrile (details being given below for **6Ln**, **7La**,**Ce** and **8Pr**), though this had the disadvantage of providing crystals containing rather diverse solvent mixtures as well as cationic or neutral complexes. Described in the following (in order of Ln) are those instances where the synthesis led to crystals suitable for structure determinations. Dmf and dmso solvates of lanthanide nitrates and perchlorates used as reactants in the syntheses were prepared by methods outlined in[21,41,42] and in references therein. Instability (primarily efflorescence) of the crystalline products if separated from their mother liquors meant that microanalyses were not be readily related to the composition estimated from the crystal structure determination and frequently not even to particular stoichiometric compositions (in which case they are not reported).

$La_4O(ClO_4)_2(L)_2\cdot 13dmf\cdot 2H_2O$ (11La): Solutions of $[La(dmf)_8](ClO_4)_3$ (280 mg) in dmf (4 mL) and ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmf (4 mL) were mixed and placed in a capped vial. A small amount of flocculent material deposited within 1 week and was filtered out. After another month, pale yellow crystals suitable for a structure determination had deposited from the filtrate. After a crystal had been selected, the bulk was collected, washed with ethanol and dried in air. Yield: 150 mg.

$La_3(OH)(NO_3)_4(LH_2)_2\cdot 4.5dmf$ (5La): Solutions of $[La(dmso)_4(NO_3)_3]$ (150 mg) in dmf (3.5 mL) and of ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.15 mL) in dmf (3.5 mL) were mixed and placed in a capped vial. After 1 month, pale yellow crystals had begun to deposit and another 4 months were then allowed for completion of this process. A crystal was selected for a structure determination, then the bulk was collected, washed with diethyl ether and dried in air. Yield: 127 mg. Microanalysis was perhaps indicative of the presence of some triethylamine and extra dmf in the bulk material: $La_3(OH)(NO_3)_4(LH_2)_2\cdot 6dmf\cdot 0.5NEt_3$ = $C_{101}H_{142.5}La_3N_{10.5}O_{27}S_8$ (2608.5): calcd. C 46.50, H 5.50, N 5.64, S 9.83; found C 47.2, H 5.6, N 5.3, S 9.5.

$(pyH)Ln_3O(NO_3)_2(LH)_2$ Solvates, Ln = La, Ce, 7La, 7Ce: Hot (90 °C) solutions of $[Ln(dmso)_4(NO_3)_3]$ (350 mg) in dmso (2 mL) and ($LH_4\cdot CHCl_3$) (200 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmso (2 mL) were mixed rapidly (using a Pasteur pipette) and then stood to cool to room temperature as a white (La) or cream (Ce) precipitate immediately began to form. After 24 h, the precipitates were collected, washed with CH_3CN, then ether, and air dried. Yields: 225 mg (La), 197 mg (Ce). Both materials proved to be completely insoluble in dmso (hot or cold) and were ultimately recrystallised from hot pyridine by vapour diffusion of a methanol/acetonitrile mixture. Their composition was deduced from the crystal structure determinations (see ahead).

$Pr_3O(NO_3)(LH)_2\cdot 16H_2O\cdot 2MeCN\cdot 5py$ (8Pr): Substitution of $[Pr(dmso)_4(NO_3)_3]$ for the $[Ln(dmso)_4(NO_3)_3]$ used in preparations of **7Ln** above and use of CH_3CN only as the diffusing solvent for the recrystallisation resulted in greenish crystals with a complex composition only fully understood through the structure determination. This composition appeared to represent that of a transitional phase between those of **7Ln** and **6Ln** (see ahead).

$Ce_3(OH)(NO_3)_4(LH_3)_2\cdot 4.5dmf$ (5Ce): A solution of $[NH_4]_2[Ce(NO_3)_6]$ (74 mg) in dmf (1 mL) was prepared as quickly as possible and immediately added to a solution of ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.15 mL) in dmf (1 mL). Although the solution formed was initially intensely violet in colour, this colour faded slowly and, after 24 h, colourless crystals mixed with but a few unsatisfactory violet crystals had been deposited. One of the colourless crystals was selected for a structure determination and the bulk colourless crystals were then collected, washed with CH_3CN and mechanically separated as much as possible from the violet material. Yield: 73 mg. This synthesis was designed for the preparation of the Ce^{IV} complex but the colourless, paramagnetic product was obviously a Ce^{III} species and similar material could also be obtained by substituting $[Ce(dmso)_4(NO_3)_3]$ for $[NH_4]_2[Ce(NO_3)_6]$ in the above procedure. Some purple material was nonetheless produced in this reaction and possibly for this reason, satisfactory analyses could not be obtained on the bulk material.

$Pr_4(OH)(NO_3)_3(L)_2\cdot 8dmf\cdot 2dmso\cdot 3H_2O$ (10Pr): Solutions of $[Pr(dmso)_4(NO_3)_3]$ (150 mg) in dmf (0.5 mL) and of ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.15 mL) in dmf (1 mL) were mixed and placed in a capped vial. After 2 months' standing, no precipitate was apparent but, after adding CH_3CN (1 mL), large green crystals deposited over the ensuing 2 months. A crystal was selected for a structure determination and the bulk precipitate was then collected, washed with diethyl ether and air dried. Yield: 100 mg. Microanalyses were consistent with the same formulation as deduced from the structure solution: $Pr_4(OH)(NO_3)_3\cdot 8dmf\cdot 2dmso\cdot 3H_2O$ = $C_{108}H_{163}N_{11}O_{31}Pr_4S_{10}$ (2995.8): calcd. C 43.30, H 5.48, N 5.14, S 10.70; found C 43.1, H 5.1, N 5.1, S 10.4.

$Nd_4O(ClO_4)_2(L)_2\cdot 11.33dmf\cdot 5H_2O$ (11Nd): Solutions of $[Nd(dmf)_8](ClO_4)_3$ (240 mg) in dmf (4 mL) and ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmf (4 mL) were mixed and placed in a capped vial. After 3 d, violet crystals suitable for a structure determination had deposited. After a crystal had been selected for this purpose, the bulk was collected, washed with ethanol and dried in air. Yield: 112 mg: $Nd_4O(ClO_4)_2(L)_2\cdot 11.33dmf\cdot 4H_2O$ = $C_{114}H_{177.67}Cl_2N_{11.33}Nd_4O_{33.33}S_8$ (3126.8): calcd. C 43.79, H 5.73, N 5.07, S 8.20; found C 44.0, H 5.6, N 4.9, S 8.0.

$Nd_3(OH)(NO_3)_4(LH_2)_2\cdot 4.5dmf$ (5Nd): Solutions of $[Nd(dmso)_4(NO_3)_3]$ (150 mg) in dmf (3 mL) and of ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.15 mL) in dmf (3 mL) were mixed and placed in a capped vial. Large purple crystals appeared within a few days and, after one had been selected for a structure determination, these were collected, washed with ethanol and air dried. Yield: 128 mg. Microanalyses were perhaps indicative of the retention of some of the wash solvent by the bulk material: $Nd_3(OH)(NO_3)_4(LH_2)_2\cdot$

$4.5dmf\cdot 2CH_3CH_2OH$ = $C_{97.5}H_{136.5}N_{8.5}Nd_3O_{27.5}S_8$ (2556.9): calcd. C 45.70, H 5.37, N 4.65, S 10.01; found C 46.3, H 5.4, N 4.2, S 9.9.

$Sm_4(OH)(NO_3)_3(L)_2\cdot 8dmf\cdot 2dmso\cdot 3H_2O$ (10Sm): Solutions of $[Sm(dmso)_4(NO_3)_3]$ (180 mg) in dmf (3.5 mL) and of ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmf (3.5 mL) were mixed and placed in a capped vial. After 1 month, colourless crystals had begun to form and one was removed from the mixture for a structure determination.

$Sm_3O(NO_3)(LH)_2\cdot 4H_2O\cdot 2dmso\cdot 2MeCN\cdot 3py$ (6Sm): Hot (90 °C) solutions of $[Sm(dmso)_4(NO_3)_3]$ (350 mg) in dmso (2 mL) and ($LH_4\cdot CHCl_3$) (200 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmso (2 mL) were mixed rapidly (using a Pasteur pipette) and then stood to cool to room temperature as a white precipitate immediately began to form. After 24 h, this was collected, washed with CH_3CN, then ether, and air dried. Yield: 217 mg. Efforts to recrystallise this material from dmso alone proved unsuccessful, so the material was analysed crude before further treatment: $Sm_3O(LH)_2(NO_3)\cdot 3dmso$ = $C_{86}H_{108}NO_{16}S_{11}Sm_3$ (2215.6): calcd. C 46.96, H 4.95, N 0.64, S 16.04; found C 47.0, H 5.6, N 0.51, S 16.6. To obtain crystals suitable for a structure determination, crude material (5 mg) was dissolved in hot (60 °C) pyridine (0.1 mL) and the solution placed in a vapour diffusion cell containing CH_3CN (2 mL). Very pale yellow tablets formed over several days.

$Sm_2(LH)_2\cdot H_2O\cdot 8dmf$ (1Sm): Solutions of $[Sm(dmso)_4(NO_3)_3]$ (120 mg) in dmf (5 mL) and of ($LH_4\cdot CHCl_3$) (25 mg) and $N(CH_2CH_3)_3$ (0.15 mL) in dmf (1 mL) were mixed and placed in a capped vial. Colourless plate-like crystals deposited over a period of 4 d. One was selected for a structure determination and the rest was collected, washed with diethyl ether and air dried. Yield: 13 mg. Microanalyses were consistent with a degree of desolvation/hydration of the bulk material: $Sm_2(LH)_2\cdot 7dmf\cdot 5H_2O$ = $C_{101}H_{149}N_7O_{20}S_8Sm_2$ (2338.6): calcd. C 51.87, H 6.42, N 4.19, S 10.97; found C 51.2, H 6.2, N 4.8, S 10.9.

$Eu_2(LH)_2\cdot 5dmf\cdot 2CH_3CN\cdot H_2O$ (1Eu): Solutions of $[Eu(dmso)_4]$-$(NO_3)_3$ (180 mg) in dmf (2 mL) and of ($LH_4\cdot CHCl_3$) (0.1 g, 0.12 mmol) in dmf (2 mL) and $N(CH_2CH_3)_3$ (0.15 mL) were mixed giving immediately a deep yellow solution. This was layered with acetonitrile and after a month crystals suitable for a structure determination were deposited. These were collected and air dried. Yield: 210 mg: $Eu_2O(LH)_2\cdot 5dmf\cdot 2CH_3CN\cdot H_2O\cdot$ = $C_{102}H_{140}Eu_2N_8O_{16}S_8$ (2294.7): calcd. C 53.38, H 6.15, N 4.88; found C 51.0, H 5.73, N 4.1.

$Eu_3O(L)(LH)(LH_4)\cdot 13dmf$ (3): Solutions of $[Eu(dmso)_8](ClO_4)_3$ (150 mg) in dmf (1 mL) and of ($LH_4\cdot CHCl_3$) (84 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmf (1 mL) were mixed. giving a deep yellow solution which was placed in a capped vial. Over several days at room temperature, orange crystals slowly deposited. These were collected, washed with diethyl ether and air dried. Yield: 97 mg: $Eu_3(OH)(L)_2(LH_4)\cdot 13dmf$ = $C_{159}H_{228}Eu_3N_{13}O_{26}S_{12}$ (3578.4): calcd. C 53.37, H 6.42, N 5.09, S 10.75; found C 53.0, H 6.2, N 4.8, S 10.3.

$Eu_6O_2(NO_3)(LH)_3(L)\cdot 11dmf\cdot dmso\cdot 5MeCN\cdot 4.75H_2O$ (4): Solutions of $[Eu(dmso)_4(NO_3)_3]$ (180 mg) in dmf (0.5 mL) and of ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.15 mL) in dmf (1 mL) were mixed and placed in a capped vial. No precipitate formed from the bright yellow solution over 1 month, so CH_3CN (2 mL) was added, causing yellow crystals mixed with some amorphous material to appear over the next 2 months. One crystal was taken for a structure determination and the others were mechanically separated from the amorphous material to provide an approximate estimate of the yield (≈ 62 mg). Satisfactory analyses could not be obtained on this impure material.

$Eu_4O(OH)_2(L)(LH_2)_2(LH_4)\cdot 12dmf$ (9): In a minor variation on the preceding experiment, solutions of $[Eu(dmso)_4(NO_3)_3]$ (178 mg) in dmf (3.5 mL) and of ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmf (3.5 mL) were mixed and placed in a capped vial. In this instance, a small number of yellow crystals formed over 1 month of standing the solution at room temperature. The total quantity obtained (≈ 3 mg) was insufficient for microanalysis.

$Eu_3O(NO_3)(LH)_2\cdot 4H_2O\cdot 2dmso\cdot 2MeCN\cdot 3py$ (6Eu): Hot (90 °C) solutions of $[Eu(dmso)_4(NO_3)_3]$ (350 mg) in dmso (2 mL) and ($LH_4\cdot CHCl_3$) (200 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmso (2 mL) were mixed rapidly (using a Pasteur pipette) and then stood to cool to room temperature as a yellow precipitate almost immediately began to form. After 24 h, this was collected, washed with CH_3CN, then ether, and air dried. Yield: 255 mg. [For the crude material, $Eu_3O(LH)_2(NO_3)\cdot 2dmso$ = $C_{84}H_{102}Eu_3NO_{14}S_{10}$ (2126.4): calcd. C 47.45, H 4.84, N 0.66; found C 47.5, H 5.5, N 0.59.] To obtain crystals suitable for a structure determination, crude material (5 mg) was dissolved in hot (60 °C) pyridine (0.1 mL) and the solution placed in a vapour diffusion cell containing CH_3CN (2 mL). Yellow tablets formed over several days.

$Dy_3O(NO_3)(LH)_2\cdot 4H_2O\cdot 2dmso\cdot 2MeCN\cdot 3py$ (6Dy): Starting with $[Dy(dmso)_3(NO_3)_3]$, an identical procedure to that described for **6Eu** provided near-colourless crystals of the Dy analogue.

$Gd_4(OH)(NO_3)_3(L)_2\cdot 8dmf\cdot 2dmso\cdot 3H_2O$ (10Gd): Solutions of $[Gd(dmso)_3(NO_3)_3]$ (180 mg) in dmf (0.5 mL) and ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.1 mL) in dmf (1 mL) were mixed and placed in a capped vial. No crystals appeared over 2 months at room temperature but, after adding CH_3CN (2 mL), large near colourless crystals appeared over the next 2 months. A crystal was selected for a structure determination, then the bulk was collected, washed with ethanol and air dried. Yield: 116 mg. Microanalysis was consistent with some hygroscopicity of the bulk material, $Gd_4(OH)L_2(NO_3)_3\cdot 8dmf\cdot 2dmso\cdot 8H_2O$ = $C_{108}H_{173}Gd_4N_{11}O_{36}S_{10}$ (3151.3): calcd. C 41.16, H 5.53, N 4.89, S 10.18; found C 41.1, H 4.8, N 4.9, S 9.3.

$Gd_4O_2(LH_2)_4\cdot 2H_2O\cdot 2MeOH\cdot dmf\cdot 3.375CH_2Cl_2$ (12): ($LH_4\cdot CHCl_3$) (0.3 g) was dissolved in dmf (3 mL) containing Et_3N (0.45 mL) and a solution of $[Gd(dmso)_4(NO_3)_3]$ (0.32 g) in dmf (1.55 mL) quickly added; the white precipitate formed (0.0647 g) was filtered off, and the filtrate placed in a freezer for several months yielding a second fraction, 0.0459 g (total yield, 31.1%). Single crystals were grown from CH_2Cl_2/MeOH. $Gd_4O_2L_4\cdot 2H_2O\cdot 2MeOH\cdot dmf\cdot 3.375CH_2Cl_2$ = $C_{168.38}H_{209.75}Cl_{6.75}Gd_4NO_{23}S_{16}$ (3996.9): calcd. C 50.6, H 5.29, N 0.35; found C 51.2, H 5.4, N 0.32.

$Yb_3(OH)_3(LH)_2\cdot 6dmf\cdot 6H_2O$ (2Yb): Solutions of $[Yb(dmso)_3$-$(NO_3)_3]$ (70 mg) in dmf (4.5 mL) and of ($LH_4\cdot CHCl_3$) (50 mg) and $N(CH_2CH_3)_3$ (0.15 mL) in dmf (3 mL) were mixed and placed in a capped vial. Needle-like crystals deposited over the ensuing 24 h and, after one had been selected for a structure determination, they were collected, washed with ethanol and air dried. Yield: 21 mg. Microanalyses indicated some desolvation/hydration of the bulk relative to the single crystal, $Yb_3(OH)_3(LH)_2\cdot 3dmf\cdot 5H_2O$ = $C_{89}H_{124}N_3O_{19}S_8Yb_3$ (2315.6): calcd. C 46.16, H 5.48, N 1.81, S 11.08; found C 46.8, H 5.1, N 1.4, S 11.1.

$Lu_3(OH)_3(LH)_2\cdot 6dmf\cdot 6H_2O$ (2Lu): Solutions of $[Lu(dmso)_3$-$(NO_3)_3]$ (160 mg) in dmf (1 mL) and of ($LH_4\cdot CHCl_3$) (100 mg) and $N(CH_2CH_3)_3$ (0.15 mL) in dmf (1 mL) were mixed and placed in a capped vial. Needle-like crystals deposited over the ensuing 24 h and, after one had been selected for a structure determination, they were collected, washed with ethanol and air dried. Yield: 50 mg. Again, microanalyses indicated different solvation of the dried bulk relative to the single crystal, $Lu_3(OH)_3(LH)_2$·5dmf·14H_2O = $C_{95}H_{156}Lu_3N_5O_{30}S_8$ (2629.7): calcd. C 43.39, H 5.98, N 2.66, S 9.76; found C 43.7, H 5.5, N 3.4, S 9.4.

$Lu_3O(NO_3)(LH)_2$·4H_2O·2dmso·2MeCN·3py (6Lu): An identical procedure to that given above for the analogous Sm, Eu and Dy compounds provided colourless crystals of the Lu complex. Note that microanalysis of the crude material obtained directly from dmso indicated that it might not have the same composition as the corresponding samples of complexes containing Sm and Eu, even though the final recrystallised materials had identical stoichiometry and structure. $Lu_3O(L)(LH)(NO_3)_2$·2dmso = $C_{84}H_{102}Lu_3N_2O_{17}S_{10}$ (2257.3): calcd. C 44.7, H 4.55, N 1.24; found C 44.0, H 5.1, N 1.2.

Structure Determinations: General procedures are described in an accompanying paper;[1] for a number of determinations, final refinements were on F^2 [all data; $I > 2\sigma(I)$], employing the SHELXL 97 program;[43] reflection weights were of the form $[\sigma^2(F^2) + (aP)^2 (+ bP)]^{-1}$ $[P = (F_o^2 + 2F_c^2)/3]$. Specific crystallographic/refinement details are given below. CCDC-656052 (**1Sm**), -668120 (**1Eu**), -656053 (**2Yb**), -656054 (**2Lu**), -656055 (**3**), -656056 (**4**), -656057 (**5La**), -656058 (**5Ce**), -656059 (**5Nd**), -656060 (**6Sm**), -656061 (**6Eu**), -743328 (**6Dy**), -656062 (**6Lu**), -743330 (**7La**), -743329 (**7Ce**), -743327 (**8**), -656063 (**9**), -656064 (**10Pr**), -656065 (**10Sm**), -656066 (**10Gd**), -656067 (**11La**), -656068 (**11Nd**), -674922 (**12**) 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.

I. Binuclear Arrays: Ln/L(1:1) Stoichiometry

1. 2Ln(LH)·H_2O·6dmf·*n*S ≡ [(μ-H_2O){Ln(*O*-dmf)$_2$}$_2$(HL·dmf)$_2$]-(·*n*dmf) (**1Ln**, Ln = Sm, Eu). Monoclinic, space group $P2_1$ (C_2^2, No. 4), $Z = 2$.

1Sm (*n*S = 2dmf)

$C_{104}H_{148}N_8O_{17}S_8Sm_2$, $M = 2339.6$. $a = 14.578(1)$, $b = 24.231(2)$, $c = 17.174(1)$ Å, $\beta = 108.822(1)°$, $V = 5742$ Å^3. $D_c = 1.35_3$ g cm^{-3}. $\mu_{Mo} = 12.2$ cm^{-1}; specimen: 0.48 × 0.14 × 0.07 mm; $T_{min./max.} = 0.86$. $2\theta_{max.} = 58°$; $N_t = 64238$, $N = 28411$ ($R_{int} = 0.036$), $N_o = 23989$; $R_1 = 0.051$, $wR_2 = 0.14$ ($a = 0.089$, $b = 1.182$). $x_{abs.} = 0.10(1)$.

Variata: Two substantial peaks in the central plane of the molecule were assigned as fragments of the samarium atoms, either disordered, or of a cocrystallised isomer, site occupancies refining to 0.9501(3) (parent components) and complements. On the basis of phenoxide *O*···*O* distances, charge balance considerations (etc.), the ligands were assigned as (LH) and the residue bridging the two samarium atoms as H_2O, the protonic hydrogen atoms not being defined in difference maps. Of the two included solvent molecules, dmf(1,2), dmf(2) was modelled as disordered over two sets of sites, occupancies set at 0.5, light atom displacement parameter form refinement isotropic.

1Eu (*n*S = 1.5dmf·2MeCN)

$C_{100.5}H_{136.5}Eu_2N_{7.5}O_{14.5}S_8$, $M = 2242.1$. $a = 14.4488(3)$, $b = 24.1118(5)$, $c = 16.8680(7)$ Å, $\beta = 108.342(3)°$, $V = 5578$ Å^3. $D_c = 1.33_5$ g cm^{-3}. $\mu_{Cu} = 9.8$ cm^{-1}; specimen: 0.26 × 0.16 × 0.055 mm; $T_{min./max.} = 0.21$. $2\theta_{max.} = 135°$; $N_t = 66305$, $N = 17379$ ($R_{int} = 0.070$), $N_o = 12525$; $R_1 = 0.066$, $wR_2 = 0.20$ ($a = 0.127$). $x_{abs.} = 0.015(3)$.

Variata: Data were measured at 100 K using monochromatic Cu-K_α radiation ($\lambda = 1.5417_8$ Å). No disorder was observed in the europium atom sites. dmf(2) was found to be disordered as before, seemingly concerted with disorder in *tert*-butyl groups 12,21,24, occupancies refining to 0.681(8) and complement (minor component displacement parameter forms isotropic). dmf(6) was assigned a site occupancy of 0.5 after trial refinement. Lattice dmf and MeCN, and disordered *tert*-butyl groups were refined with idealised geometries.

II. Trinuclear Arrays

(a) Without Oxyanion Component

(i) Equilateral Triangular Ln_3O Arrays

$Ln(OH)_3$·2Ln(LH)·*x*dmf·*y*H_2O ≡ [(H*O*)$_3${Ln(*O*H_2)}$_2${Ln(*O*-dmf)}-(HL·dmf)$_2$][·(*x* – 3)dmf·(*y* – 2)H_2O] (2Ln) (Ln = Yb, Lu): Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $Z = 4$.

2Yb (*x* = 6, *y* = 6): $C_{99}H_{147}N_6O_{22.5}S_8Yb_3$, $M = 2544.8$. $a = 21.702(2)$, $b = 23.056(3)$, $c = 29.079(3)$ Å, $\alpha = 98.942(2)$, $\beta = 98.066(2)$, $\gamma = 115.201(1)°$, $V = 12653$ Å^3. $D_c = 1.33_6$ g cm^{-3}. $\mu_{Mo} = 24$ cm^{-1}; specimen: 0.38 × 0.35 × 0.17 mm; $T_{min./max.} = 0.63$. $2\theta_{max.} = 50°$; $N_t = 138198$, $N = 44535$ ($R_{int} = 0.056$), $N_o = 36210$; $R_1 = 0.12$, $wR_2 = 0.28$ ($a = 0.034$, $b = 840$).

2Lu (*x* ≈ 6.5, *y* ≈ 5.5): $C_{99.5}H_{149.5}Lu_3N_{6.5}O_{23}S_8$, $M = 2586.2$. $a = 21.625(2)$, $b = 23.016(2)$, $c = 29.190(2)$ Å, $\alpha = 99.066(2)$, $\beta = 98.255(2)$, $\gamma = 115.020(1)°$, $V = 12637$ Å^3. $D_c = 1.35_9$ g cm^{-3}. $\mu_{Mo} = 25$ cm^{-1}; specimen: 0.25 × 0.10 × 0.05 mm; $T_{min./max.} = 0.77$. $2\theta_{max.} = 50°$; $N_t = 122288$, $N = 44478$ ($R_{int} = 0.067$), $N_o = 27419$; $R_1 = 0.084$, $wR_2 = 0.23$ ($a = 0.098$, $b = 163$).

Variata: Hydroxylic hydrogen atoms were not located in either structure. Difference map residues were modelled as dmf (#3–6, 7 being refined with constrained geometries and isotropic displacement parameters forms) or H_2O oxygen (isotropic forms also, site occupancies 0.5 or 1). *tert*-butyl groups 2114, 2224 were modelled as rotationally disordered over two sets of sites about their pendants, site occupancies 0.5.

(ii) Isosceles Triangular Ln_3O Arrays

$Eu_3O(L)(LH)(LH_4)$·13dmf ≡ [*O*{Eu(*O*-dmf)$_2$}$_3$(L·dmf)(HL·dmf)]-(H_4L·dmf)·4dmf (3)

$C_{159}H_{228}Eu_3O_{26}N_{13}S_{12}$, $M = 3578.3$. Triclinic, space group $P\bar{1}$, $a = 15.711(1)$, $b = 21.850(2)$, $c = 27.100(2)$ Å, $\alpha = 81.592(1)$, $\beta = 84.001(1)$, $\gamma = 77.226(1)°$, $V = 8950$ Å^3. D_c ($Z = 2$) = 1.32_8 g cm^{-3}. $\mu_{Mo} = 12.4$ cm^{-1}; specimen: 0.67 × 0.35 × 0.08 mm; $T_{min./max.} = 0.76$. $2\theta_{max.} = 58°$; $N_t = 107005$, $N = 43658$ ($R_{int} = 0.053$), $N_o = 26146$; $R_1 = 0.065$, $wR_2 = 0.18$ ($a = 0.047$, $b = 52$).

Variata: Dmf molecules 3–5 were refined with isotropic displacement parameter forms for C, N, O and idealised geometries.

(b) With Oxyanion Component: Isosceles Triangular Ln_3O Arrays

$Eu_6O_2(NO_3)(LH)_3(L)$·11dmf·dmso·5MeCN·4.75H_2O ≡ [O{Eu(*O*-dmf)(*N*CMe)}{Eu(*O*NO_2) (*O*-dmf)}{Eu(*O*-dmf)$_2${(HL·NCMe)$_2$}]-[O{Eu(*O*-dmf)$_2$}{Eu(*O*-dmf)(*O*-dmso)}{Eu(*O*-dmf)(*N*CMe)}(HL·NCMe)(L·NCMe)](·3dmf·4.75H_2O) (4)

$C_{207}H_{289.5}Eu_6N_{18}O_{37}S_{17}$, $M = 5078.9$. Triclinic, space group $P\bar{1}$, $a = 20.175(2)$, $b = 26.704(2)$, $c = 27.047(2)$ Å, $\alpha = 68.020(2)$, $\beta = 70.461(2)$, $\gamma = 69.981(2)°$, $V = 12335$ Å^3. D_c ($Z = 2$) = 1.36_7 g cm^{-3}. $\mu_{Mo} = 17.1$ cm^{-1}; specimen: 0.25 × 0.20 × 0.10 mm; $T_{min./max.} = 0.65$. $2\theta_{max.} = 58°$; $N_t = 136691$, $N = 60540$ ($R_{int} = 0.074$), $N_o = 30291$; $R_1 = 0.088$, $wR_2 = 0.32$ ($a = 0.185$, $b = 1.58$).

Variata: Despite the complexity of the model and some high displacement parameters, plausible modelling of the components of the substrate molecules was straightforward. The lattice solvent molecules were less so, dmf 10–40 being modelled as disordered, the components of these and of “water molecule oxygen” residues O(03–09) being modelled with site occupancies 0.5.

$\mathrm{Ln_3(OH)(NO_3)_4(LH_2)_2\cdot 4.5dmf} \equiv \mathrm{[(H}O\mathrm{)\{Ln(}O\mathrm{NO_2)_2\}\{Ln(}O\mathrm{NO_2)(}O\mathrm{\text{-}dmf)\}_2(H_2L\cdot dmf)_2](\cdot 0.5dmf)}$ (5Ln)

$\mathrm{C_{93.5}H_{124.5}Ln_3N_{8.5}O_{25.5}S_8}$, Ln = La, Ce, Nd. Monoclinic, space group *C*2/*m* ($C_{2h}{}^3$, No. 12), *Z* = 2.

5La: M = 2448.8. a = 17.050(1), b = 23.176(2), c = 14.796(1) Å, β = 108.909(1)°, V = 5531 Å^3. $D_c = 1.47_0$ g cm^{-3}. μ_{Mo} = 13.6 cm^{-1}; specimen: 0.55 × 0.25 × 0.16 mm; $T_{min./max.}$ = 0.67. $2\theta_{max.}$ = 58°; N_t = 26447, N = 7094 (R_{int} = 0.027), N_o = 6069; R = 0.074, R_w = 0.089.

5Ce: M = 2452.5. a = 17.087(2), b = 23.129(3), c = 14.802(2) Å, β = 109.255(2)°, V = 5523 Å^3. $D_c = 1.47_5$ g cm^{-3}. μ_{Mo} = 14.4 cm^{-1}; specimen: 0.44 × 0.40 × 0.15 mm; $T_{min./max.}$ = 0.73. $2\theta_{max.}$ = 50°; N_t = 30160, N = 4913 (R_{int} = 0.042), N_o = 4146; R = 0.082, R_w = 0.099.

5Nd: M = 2464.8. a = 17.048(2), b = 23.087(3), c = 14.793(2) Å, β = 109.380(2)°, V = 5492 Å^3. $D_c = 1.49_0$ g cm^{-3}. μ_{Mo} = 16.2 cm^{-1}; specimen: 0.35 × 0.30 × 0.16 mm; $T_{min./max.}$ = 0.80. $2\theta_{max.}$ = 58°; N_t = 26597, N = 7057 (R_{int} = 0.029), N_o = 5677; R = 0.079, R_w = 0.096.

***Variata*:** *C*2/*m* is one of the more frequently misassigned space groups and its occurrence in the present context immediately raises questions of that type, which, in the present situation, we have been unable to find any more satisfactory resolution of. Data quality is among the best of the present array of structural studies, with no primitive- or super-lattice data observed, and no satisfactory model of lower symmetry. The macrocycle (inclusive of *tert*-butyl pendants) is generally well-ordered, refining normally, the included dmf 20 disordered over two sites, occupancies set at 0.75, 0.25 after trial refinement; *O*···*O* distances within the ligand are generally long, suggestive of complete deprotonation, the most likely location for the proton required for charge balance within a presumedly neutral aggregate being in conjunction with the core oxygen atom, which is essentially coplanar with the three Ln atoms. In *C*2/*m*, that oxygen is disposed on a crystallographic symmetry element, entailing symmetry of $2/m//\bar{1}$ for the aggregate, i.e. entailing disorder in the $\mathrm{Ln_3}$ core within an ordered envelope of the pair of macrocycles which are comfortably related in that manner, although the nitrate groups, also disordered, were refined with idealised geometries, as were the other (disordered) dmf molecules, the components of which were assigned site occupancies 0.5 and isotropic displacement parameter forms in refinement. Following the introduction of pyridine (py), **6Ln**, **7Ln**, and **8** were obtained:

$\mathrm{Ln_3O(NO_3)(LH)_2\cdot 4H_2O\cdot 2dmso\cdot 2MeCN\cdot 3py} \equiv [O\mathrm{\{Ln(}O\mathrm{\text{-}dmso)(py)\}_2\{Ln(}O\mathrm{H_2)(}O\mathrm{NO_2)\}(HL\cdot NCMe)_2](\cdot py\cdot 3H_2O)}$ (6Ln)

$\mathrm{C_{103}H_{131}LnN_6O_{18}S_{10}}$, Ln = Sm, Eu, Lu. Monoclinic, space group $P2_1/n$ ($C_{2h}{}^5$, No. 14)(variant), *Z* = 2.

6Sm: M = 2513.0. a = 13.8761(9), b = 23.767(2), c = 17.761(1) Å, β = 90.209(2)°, V = 5857 Å^3. $D_c = 1.42_5$ g cm^{-3}. μ_{Mo} = 17.2 cm^{-1}; specimen: 0.20 × 0.07 × 0.07 mm; $T_{min./max.}$ = 0.83. $2\theta_{max.}$ = 64°; N_t = 74293, N = 19435 (R_{int} = 0.079), N_o = 10594; R = 0.072, R_w = 0.079.

6Eu: M = 2517.8. a = 13.8179(8), b = 23.634(1), c = 17.734(1) Å, β = 90.647(1)°, V = 5791 Å^3. $D_c = 1.44_4$ g cm^{-3}. μ_{Mo} = 18.5 cm^{-1}; specimen: 0.40 × 0.18 × 0.11 mm; $T_{min./max.}$ = 0.86. $2\theta_{max.}$ = 66°; N_t = 83969 N = 21457 (R_{int} = 0.047), N_o = 14762; R = 0.064, R_w = 0.075.

6Dy: M = 2531.2. a = 13.8354(8), b = 23.657(1), c = 17.693(1) Å, β = 89.625(1)°, V = 5791 Å^3. $D_c = 1.45_2$ g cm^{-3}. μ_{Mo} = 21.6 cm^{-1}; specimen: 0.18 × 0.06 × 0.05 mm; $T_{min./max.}$ = 0.79. $2\theta_{max.}$ = 58°; N_t = 57207 N = 14973 (R_{int} = 0.074), N_o = 10674; R_1 = 0.11, wR_2 = 0.29.

6Lu: M = 2586.8 a = 13.862(2), b = 23.523(3), c = 17.686(2) Å, β = 89.634(2)°, V = 5767 Å^3. $D_c = 1.49_0$ g cm^{-3}. μ_{Mo} = 28 cm^{-1}; specimen: 0.12 × 0.06 × 0.05 mm; $T_{min./max.}$ = 0.67. $2\theta_{max.}$ = 55°; N_t = 54511, N = 13277 (R_{int} = 0.13), N_o = 6359; R = 0.077, R_w = 0.085.

***Variata*:** The peculiarities experienced with this family of structures of complexes achieved with rare earths, Ln = Sm and beyond, mirror those of **5Ln**, obtained for Ln = Nd and preceding elements. While the complexes are very different in respect of anion complement other than (LH) and consequent proton distribution, the similarity in cell dimensions of the two series is suggestive of considerable similarity in gross crystal packing despite the modelling of one array in *C*2/*m* and the other $P2_1/n$ (note the interchange of *a* and *c*); the tilting of the complex aggregate necessary to transform the one into the other is clearly seen in the unit cell projections of the two arrays given in Figure 5, (b) and 6, (a), the diverse anionic and solvent components being accommodated in the voids in the structure, as well as in the equatorial plane of the coordination sphere. Here, again with better quality data (especially for the Eu complex), we find the same disconcerting disorder of the molecular core, incompatible with the space group, first of all by inversion of the $\mathrm{Ln_3}$ array through the core oxygen atom, located at the inversion centre, and, beyond that, by rotation of the $\mathrm{Ln_3}$ core through ninety degrees, so that refinement of site occupancies of Ln(1,2) yield x_1 = 0.8917(7), 0.8967(6), 0.932(1) (Ln = Sm, Eu, Lu) with $x_2 = 1.5 - x_1$; the difference being minor, complementary assignments were not made to the occupancies of the ligands about sites 1, 2, those at Ln(1) ($\mathrm{OH_2}$ and $\mathrm{ONO_2}$) and at Ln(2) (py, dmso) being disordered as well, seemingly 50:50, which constraint was applied, with rigid body and isotropic displacement parameter refinement. Pyridine groups 2,3 were modelled with similar constraints, as also *tert*-butyl groups 34, 44, rotationally disordered over two sets of sites of equal occupancy, while *tert*-butyl 24 was modelled over sites refining to occupancies 0.783(1), 0.793(1), 0.65(2) and complements. Geometries are given for the extremal **6Sm**, **Lu** in Table S8, those for **6Eu** and **6Dy** (see below) being available from the CIF depositions. Refinement of **6Dy** was executed on F^2 using SHELXL 97 some time after the Sm/Eu/Lu triad and found to display no disorder; as a check, rerefinement of the Sm complex in that manner produced no non-trivial change to the previous model. Crystals of pyridine adducts were also obtained with similar crystal system and cell dimensions, albeit with models with somewhat different formulations and degrees of disorder for Ln = La, Ce in space group *Pn*, as presented below (**7Ln**). An adduct was also obtained for Ln = Pr but of a unique unrelated form (**8**), without core disorder.

$\mathrm{(pyH)Ln_3O(NO_3)_2(LH)_2\cdot}x\mathrm{H_2O\cdot}y\mathrm{dmso\cdot 2MeCN\cdot 1.5py\cdot MeOH} \equiv \mathrm{(pyH)_{(2|2)}[O\{Ln^{a}(}O_2\mathrm{NO)(py)_{0.5}\}\{Ln^{b}L^{x}\}\{Ln^{c}(}O_2\mathrm{NO)(py)_{0.5}\}\{Ln^{d}(}O\mathrm{\text{-}dmso)_{y}L^{y}\}(HL\cdot MeCN)_2]\cdot}x\mathrm{H_2O}$ (7Ln): Monoclinic, space group *Pn* ($C_s{}^2$, No. 7 variant), *Z* = 2.

7La: [L^x = MeOH, L^y = (1/2py + 1/2dmso); x = 6/2, y = 3/2]: $\mathrm{C_{100.5}H_{134.5}La_3N_{6.5}O_{20.5}S_{9.5}}$, M = 2482.9. a = 13.990(2), b = 23.687(3), c = 17.831(2) Å, β = 90.226(3)°, V = 5909 Å^3. $D_c = 1.39_2$ g cm^{-3}. μ_{Mo} = 13.9 cm^{-1}; specimen: 0.20 × 0.06 × 0.05 mm; $T_{min./max.}$ = 0.52. $2\theta_{max.}$ = 55°; N_t = 54417, N = 13580 (R_{int} = 0.13), N_o = 8067; R_1 = 0.12, wR_2 = 0.34 (a = 0.175, b = 55). $x_{abs.}$ = 0.09(4).

7Ce: (L^x = *O*-dmso, L^y = MeOH; x = 4/2, y = 2/2): $\mathrm{C_{102}H_{130}Ce_3N_7O_{19}S_9}$, M = 2467.0. a = 13.991(2), b = 23.811(4), c = 17.832(3) Å, β = 90.380(3)°, V = 5940 Å^3. $D_c = 1.37_7$ g cm^{-3}. μ_{Mo}

= 13.5 cm^{-1}; specimen: 0.30 × 0.10 × 0.05 mm; $T_{\text{min./max.}}$ = 0.70. $2\theta_{\text{max.}}$ = 58°; N_t = 57297, N = 28456 (R_{int} = 0.072), N_o = 16506; R_1 = 0.090, wR_2 = 0.25 (a = 0.13, b = 8.0). $x_{\text{abs.}}$ = 0.10(2).

Variata: In both of these complexes, the lanthanoid atom complement is distributed over four sites; site occupancies were refined within a total population of 3, resulting in (1–4; La; Ce) [0.954(6), 0.351(6), 0.898(6), 0.796(6); 0.826(3), 0.899(3), 0.834(3), 0.445(3)]; release of the total constraint of 3 resulted in no non-trivial divergence from that sum. In both complexes, Ln^a [= Ln(1)] is coordinated by a bidentate nitrate group and the nitrogen atom of a half-weighted pyridine molecule (U forms isotropic in refinement). Ln^b [= Ln(2)] is coordinated by MeOH in the La complex, dmso in the Ce complex; in both compounds, both molecules are modelled as disordered over two sets of sites, of equal occupancy in the case of the methanol, in the case of the dmso of sites of occupancy 0.689(8) and complement, pendant from a single coordinated oxygen site, which corresponds to one of the methanol half-oxygen sites, the other being shared by the nitrogen atom of a coordinated pyridine (U of the disordered components isotropic throughout). Ln^c [= Ln (3)] is coordinated by a bidentate nitrate group and a half-weighted pyridine. Ln^d [= Ln (4)] is coordinated by a pair of half-weighted methanol components in the Ln = Ce complex; in the Ln = La complex a fully occupied dmso oxygen atom (the remainder of the dmso disordered) and (superimposed) a half-weighted dmso oxygen atom (with pendant ligand) and a half-weighted pyridine (all disordered component U isotropic). Most of the *tert*-butyl groups are modelled as rotationally disordered about their pendant bonds in terms of major and minor (complementary) components [occupancies (major component): **7La** 11/0.82(5), 12/0.82(10), 13/0.79(4) (all concerted?); 22/0.79(12), 23/0.5, 24/0.75(3); **7Ce** 11,12,21,23/0.5] (U_{iso} throughout).

$Pr_3O(NO_3)(LH)_2\cdot16H_2O\cdot2MeCN\cdot5py$ ≡ [*O*{Pr^a(*O*NO$_2$)(py)$_{(0.67|0.33)}$}{Pr^b(*O*H$_2$)(py)$_{(0.5|0.5)}$}{Pr^c(*O*-dmso)(py)$_{(0.33|0.67)}$}(HL·MeCN)$_2$]·(3+24/2)H$_2$O)·2py (8)

$C_{111}H_{187}N_8O_{28}Pr_3S_9$, M = 2792.7. Monoclinic, space group $P2_1/n$ ($C_{2h}{}^5$, No. 14 variant), a = 20.448(5), b = 18.961(3), c = 30.309(5) Å, β = 98.850(3)°, V = 15018 Å^3. D_c (Z = 4) = 1.22_2 g cm^{-3}. μ_{Mo} = 11.4 cm^{-1}; specimen: 0.45 × 0.30 × 0.24 mm; $T_{\text{min./max.}}$ = 0.62. $2\theta_{\text{max.}}$ = 55°; N_t = 99399, N = 29827 (R_{int} = 0.11), N_o = 13916; R_1 = 0.13, wR_2 = 0.40 (a = 0.15, b = 370).

Variata: Pr^a = Pr(1) is coordinated by a unidentate nitrate oxygen atom and a pyridine molecule disordered over two sets of sites, occupancies 0.5. Pr^b = Pr(2) is coordinated by a water molecule oxygen atom (hydrogen atoms located, fixed) and a pyridine molecule disordered over two sets of sites, occupancies 0.5. Pr^c = Pr(3) is coordinated by an ordered *O*-dmso and a pyridine molecule disordered over two sets of sites, occupancies 0.67/0.33. Most of the *tert*-butyl groups are modelled as rotationally disordered about their pendant bonds in terms of (major and minor) (complementary) components [occupancies (major component): 11,14/0.5, 12/0.67, 13/0.75; 21,22,23/0.5]. (disordered component U isotropic throughout in refinement).

III. Tetranuclear [(Quasi-)square Ln$_4$ (O or OH)] Arrays

(a) Without Oxyanion Component

$Eu_4O(OH)_2(L)(LH_2)_2(LH_4)\cdot12dmf$ ≡ [*O*(H*O*)$_2${Eu(*O*-dmf)}$_4$(L·dmf)(LH$_2$·dmf)$_2$](LH$_4$·dmf)(·4dmf) (9)

$C_{196}H_{270}Eu_4N_{12}O_{31}S_{16}$, M = 4411.3. Orthorhombic, space group *Pnma* ($D_{2h}{}^{16}$, No. 62), a = 35.449(3), b = 34.175(6), c = 18.006(5) Å, V = 21814 Å^3. D_c (Z = 4) = 1.34_3 g cm^{-3}. μ_{Mo} = 13.5 cm^{-1}; specimen: 0.40 × 0.20 × 0.10 mm; $T_{\text{min./max.}}$ = 0.64. $2\theta_{\text{max.}}$ = 58°; N_t = 212751, N = 29010 (R_{int} = 0.13), N_o = 17311; R = 0.080, R_w = 0.091.

Variata: Although hydrogen atoms were not located, assignment is relatively straightforward in terms of macrocycle O···O distances and coordination mode. *tert*-butyl groups 13, 22 were modelled as disordered over pairs of sites, occupancies set at 0.5 after trial refinement (13), 22 being disposed about a mirror plane. All dmf groups except 30, 60, 70 were modelled as disordered over pairs of sites, occupancies 0.5. Disordered non-hydrogen atom components were refined with isotropic displacement parameter forms, geometries being constrained at idealised values.

(b) With Oxyanion Component

$Ln_4(OH)(NO_3)_3(L)_2\cdot8dmf\cdot2dmso\cdot3H_2O$ ≡ [(H*O*){Ln(*O*-dmso)(*O*-dmf)}$_2${Ln(*O*-dmf)$_2$}(L·dmf)$_2$](NO$_3$)$_3$(·3H$_2$O·2dmf) (10Ln): $C_{108}H_{163}Ln_4N_{11}O_{31}S_{10}$, Ln = Pr, Sm, Gd. Monoclinic, space group $P2_1/n$, Z = 2. The array has been previously defined for Ln = Nd [5], the present analogues being presented in the same cell and coordinate setting.

10Pr: M = 2995.8. a = 14.793(1), b = 27.864(2), c = 16.227(1) Å, β = 106.192(1)°, V = 6424 Å^3. D_c = 1.54_9 g cm^{-3}. μ_{Mo} = 17.3 cm^{-1}; specimen: 0.35 × 0.35 × 0.20 mm; $T_{\text{min./max.}}$ = 0.83. $2\theta_{\text{max.}}$ = 58°; N_t = 70805, N = 16324 (R_{int} = 0.030), N_o = 14007; R = 0.043, R_w = 0.066.

10Sm: M = 3033.6. a = 14.769(2), b = 27.690(3), c = 16.248(3) Å, β = 105.698(3)°, V = 6397 Å^3. D_c = 1.57(5) g cm^{-3}. μ_{Mo} = 20.5 cm^{-1}; specimen: 0.25 × 0.22 × 0.20 mm; $T_{\text{min./max.}}$ = 0.76. $2\theta_{\text{max.}}$ = 75°; N_t = 120548, N = 32643 (R_{int} = 0.069), N_o = 23577; R = 0.050, R_w = 0.060.

10Gd: M = 3061.2. a = 14.685(2), b = 27.646(3), c = 16.288(2) Å, β = 105.387(2)°, V = 6376 Å^3. D_c = 1.59_4 g cm^{-3}. μ_{Mo} = 23 cm^{-1}; specimen: 0.24 × 0.18 × 0.15 mm; $T_{\text{min./max.}}$ = 0.73. $2\theta_{\text{max.}}$ = 58°; N_t = 70298, N = 16258 (R_{int} = 0.026), N_o = 14104; R = 0.038, R_w = 0.051.

Variata: Hydroxylic hydrogen atoms were not located or included. *tert*-butyl group 34 was modelled as rotationally disordered about its pendant bond over two sets of sites, occupancies set at 0.5 after trial refinement. Nitrate 2 was modelled as disordered over two sets of sites, occupancies 0.5; all disordered components were refined with isotropic displacement parameter forms. A difference map residue was modelled as water molecule oxygen O(02), site occupancy 0.5. Geometries of the extremal Ln = Pr, Gd arrays are given in Table S9, that for the Sm array available from the CIF deposition. The dmso was modelled as disordered about the pendant O in the Ln = Pr adduct, not so in the others.

$Ln_4O(ClO_4)_2(L)_2\cdot x\text{dmf}\cdot yH_2O$ ≡ [*O*{Ln(*O*-dmf)$_2$}$_4$(L·dmf)$_2$](ClO$_4$)$_2$[·(x – 10)dmf·yH$_2$O] (11Ln): Monoclinic, space group $P2_1/n$, Z = 2.

11La (x = 13, y = 2): $C_{119}H_{183}Cl_2La_4N_{13}O_{32}S_8$, M = 3190.9. a = 15.189(1), b = 16.769(2), c = 29.189(3) Å, β = 95.775(2)°, V = 7397 Å^3. D_c = 1.43(3) g cm^{-3}. μ_{Mo} = 13.5 cm^{-1}; specimen: 0.30 × 0.20 × 0.15 mm; $T_{\text{min./max.}}$ = 0.83. $2\theta_{\text{max.}}$ = 58°; N_t = 71607, N = 18782 (R_{int} = 0.033), N_o = 15097; R = 0.055, R_w = 0.070.

11Nd (x = 11^1/$_3$, y = 5): $C_{114}H_{177.3}Cl_2N_{11.3}Nd_4O_{33.3}S_8$, M = 3144.5. a = 15.037(2), b = 16.790(2), c = 28.920(3) Å, β = 95.798(2)°, V = 7264 Å^3. D_c = 1.43(8) g cm^{-3}. μ_{Mo} = 16.3 cm^{-1}; specimen: 0.35 mm cuboid; $T_{\text{min./max.}}$ = 0.78. $2\theta_{\text{max.}}$ = 58°; N_t = 69853, N = 18280 (R_{int} = 0.034), N_o = 14673; R = 0.058, R_w = 0.073.

Variata: Modelling of the variety of lattice residues in terms of solvent, H$_2$O, etc. was problematic and resolved for the two compounds in total as shown with extensive disordered and varied site occupancies, and isotropic displacement parameter refinement and constrained geometries, all compensating for an inability to convincingly locate $ClO_4(1)$ at all in the Nd structure! In addition, $ClO_4(2)$ is disordered. Despite all this, data quality and associated residuals are surprisingly good, among the best in the present series of studies.

IV Other tetranuclear arrays

$Gd_4O_2(LH_2)_4{\cdot}2H_2O{\cdot}2MeOH{\cdot}dmf{\cdot}3.375CH_2Cl_2 \equiv [Gd_4O_2(LH_2)_2(LH_2{\cdot}CH_2Cl_2)_2(OH_2)_2(HOMe)_2(O\text{-}dmf)]{\cdot}(1.375CH_2Cl_2)$ (12)

$C_{168.38}H_{209.75}Cl_{6.75}Gd_4NO_{23}S_{16}$, $M = 3996.9$. Triclinic, space group $P\bar{1}$, $a = 18.1293(1)$, $b = 23.6110(10)$, $c = 24.3270(10)$ Å, $\alpha = 80.351(4)$, $\beta = 84.313(4)$, $\gamma = 69.904(5)$°, $V = 9631$ Å^3. D_c $(Z = 2) = 1.37(8)$ g cm^{-3}. $\mu_{Cu} = 11.7$ cm^{-1}; specimen: $0.09 \times 0.09 \times 0.03$ mm; $T_{min./max.} = 0.55$. $2\theta_{max.} = 140°$; $N_t = 110100$, $N = 33881$ ($R_{int} = 0.16$), $N_o = 9794$; $R_1 = 0.086$, $wR_2 = 0.23$ ($a = 0.073$).

***Variata*:** Crystals were very small and the body of very weak data was obtained at 100 K using monochromatic Cu-K_α radiation. The ad hoc protonation assignment of the ligands and solvent molecules is based on geometrical rather than difference map or refinement evidence. Of the ligands, calix (1) is empty, calyces (2,3) each contain non-disordered CH_2Cl_2 molecules, calix (4) "self-includes"("hermaphroditically") a *tert*-butyl group from an inversion related calix (4); the chlorine atoms of CH_2Cl_2 (3) were modelled as disordered over three sets of sites, occupancies set at 0.75, 0.5 after trial refinement; the site occupancy of CH_2Cl_2 (4) was similarly set at 0.5, all lattice CH_2Cl_2 molecular geometries being held at idealised values. Although none of the *tert*-butyl groups were modelled as disordered, those appended at C(114,134,224,234,324,344,444) were refined with isotropic displacement parameter forms.

Supporting Information (see footnote on the first page of this article): Tables S1–S14, giving descriptors of ligand and metal atom geometry.

Acknowledgments

Support from the since extinguished Special Research Centre for Advanced Mineral and Materials Processing and Crystallography Centre of the University of Western Australia is gratefully recorded.

---

[1] A. Bilyk, J. W. Dunlop, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. A. Koutsantonis, I. W. Murray, B. W. Skelton, A. H. White, *Eur. J. Inorg. Chem.* **2010**, 2089–2105 (Part II).

[2] A. Bilyk, J. W. Dunlop, R. O. Fuller, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. A. Koutsantonis, I. W. Murray, B. W. Skelton, R. L. Stamps, A. H. White, *Eur. J. Inorg. Chem.* **2010**, 2106–2126, preceding paper (Part III).

[3] A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton, A. H. White, *Inorg. Chem.* **2001**, *40*, 672 (Part I: *Systematic Structural Coordination Chemistry of p-tert-Butyltetrathiacalix[4]arene: 1. Group 1 Elements and Congeners*).

[4] G. Mislin, E. Graf, M. W. Hosseini, A. Bilyk, A. K. Hall, J. M. Harrowfield, B. W. Skelton, A. H. White, *Chem. Commun.* **1999**, 373.

[5] A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton, A. H. White, *Aust. J. Chem.* **2000**, *53*, 895.

[6] A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. Mislin, B. W. Skelton, C. Taylor, A. H. White, *Eur. J. Inorg. Chem.* **2000**, 823.

[7] Z. Asfari, A. Bilyk, J. W. Dunlop, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton, A. H. White, *Angew. Chem. Int. Ed.* **2001**, *40*, 721.

[8] H. Akdas, E. Graf, M. W. Hosseini, A. De Cian, A. Bilyk, B. W. Skelton, G. A. Koutsantonis, I. W. Murray, J. M. Harrowfield, A. H. White, *Chem. Commun.* **2002**, 1042.

[9] N. Morohashi, F. Narumi, N. Iki, T. Hattori, S. Miyano, *Chem. Rev.* **2006**, *106*, 5291.

[10] J. M. Harrowfield, G. A. Koutsantonis in *Calixarenes in the Nanoworld* (Eds.: L. Baklouti, J. M. Harrowfield, J. Vicens), Springer, Dordrecht, **2007**, ch. 10, p. 197.

[11] T. Kajiwara, N. Iki, M. Yamashita, *Coord. Chem. Rev.* **2007**, *251*, 1734.

[12] T. Kajiwara, H. Wu, T. Ito, N. Iki, S. Miyano, *Angew. Chem. Int. Ed.* **2004**, *43*, 1832.

[13] T. Kajiwara, K. Katagiri, S. Takaishi, M. Yamashita, N. Iki, *Chem. Asian J.* **2006**, *1*, 349.

[14] N. Iki, M. Ohta, T. Tanaka, T. Horiuchi, H. Hoshino, *New J. Chem.* **2009**, *33*, 23.

[15] N. Iki, M. Ohta, T. Horiuchi, H. Hoshino, *Chem. Asian J.* **2008**, *3*, 849.

[16] a) M. W. Hosseini in *Calixarenes 2001* (Eds.: Z. Asfari, V. Böhmer, J. M. Harrowfield, J. Vicens), Kluwer Academic Publishers, Dordrecht, **2001**, ch. 6, pp. 110ff; b) E. B. Brouwer, G. D. Enright, C. I. Ratcliffe, J. A. Ripmeester, K. D. Udachin in *Calixarenes 2001* (Eds.: Z. Asfari, V. Böhmer, J. M. Harrowfield, J. Vicens), Kluwer Academic Publishers, Dordrecht, **2001**, ch. 16, pp. 296ff; c) A. Arduini, A. Pochini, A. Secchi, F. Ugozzoli in *Calixarenes 2001* (Eds.: Z. Asfari, V. Böhmer, J. M. Harrowfield, J. Vicens), Kluwer Academic Publishers, Dordrecht, **2001**, ch. 25, pp. 457ff; d) P. Thuéry, M. Nierlich, J. M. Harrowfield, M. I. Ogden in *Calixarenes 2001* (Eds.: Z. Asfari, V. Böhmer, J. M. Harrowfield, J. Vicens), Kluwer Academic Publishers, Dordrecht, **2001**, ch. 30, pp. 561ff.

[17] M. W. Hosseini in *Calixarenes for Separations, ACS Symposium Series No. 557* (Eds.: G. J. Lumetta, R. D. Rogers, A. S. Gopalan), American Chemical Society, Washington, **2000**, p. 296.

[18] Z. Asfari, A. Bilyk, C. Bond, J. M. Harrowfield, G. A. Koutsantonis, N. Lengkeek, M. Mocerino, B. W. Skelton, A. N. Sobolev, S. Strano, J. Vicens, A. H. White, *Org. Biomol. Chem.* **2004**, *2*, 387 and references cited therein.

[19] a) V. A. Igonin, S. V. Lindeman, Yu. T. Struchkov, Yu. A. Moldotsova, O. I. Shchegolikhina, Yu. A. Podzniakova, A. A. Zhdanov, *Russ. Chem. Bull.* **1993**, *42*, 168; V. A. Igonin, S. V. Lindeman, Yu. T. Struchkov, Yu. A. Moldotsova, O. I. Shchegolikhina, Yu. A. Podzniakova, A. A. Zhdanov, *Russ. Chem. Bull.* **1993**, *42*, 176; b) O. I. Shchegolikhina, Yu. A. Podzniakova, S. V. Lindeman, A. A. Zhdanov, R. Psaro, R. Ugo, G. Gavioli, R. Battistuzzi, M. Borsari, T. Ruffer, C. Zucchi, G. Pályi, *J. Organomet. Chem.* **1996**, *514*, 29.

[20] J. M. Harrowfield, D. Matt, *J. Inclusion Phenom. Macrocyclic Chem.* **2004**, *50*, 133.

[21] J. M. Harrowfield, B. W. Skelton, A. H. White, F. R. Wilner, *Inorg. Chim. Acta* **2004**, *357/8*, 2358 and references cited therein.

[22] a) R. D. Hancock, A. E. Martell, *Chem. Rev.* **1989**, *89*, 1875; b) R. D. Hancock, *J. Chem. Educ.* **1992**, *69*, 615.

[23] J-C. G. Bünzli, J. M. Harrowfield in *Calixarenes – A Versatile Class of Macrocyclic Compounds* (Eds.: V. Böhmer, J. Vicens), Kluwer Academic Publishers, Dordrecht, **1990**, p. 211.

[24] L. M. Engelhardt, B. M. Furphy, J. M. Harrowfield, D. L. Kepert, A. H. White, F. R. Wilner, *Aust. J. Chem.* **1988**, *41*, 1465.

[25] a) R. D. Rogers, C. B. Bauer in *Comprehensive Supramolecular Chemistry, Vol. 1* (Ed.: G. W. Gokel), Pergamon, Oxford, **1996**, ch. 8, p. 315; b) L. I. Semenova, A. H. White, *Aust. J. Chem.* **1999**, *52*, 571 and references cited therein.

[26] E. N. Rizkalla, G. R. Choppin in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 15* (Eds.: K. A. Gschneidner Jr., L. Eyring), Elsevier-North Holland, **1991**, ch. 103, p. 393.

[27] E. Pedersen, *Acta Chem. Scand.* **1970**, *24*, 3362.

[28] D. M. Homden, C. A. Redshaw, *Chem. Rev.* **2008**, *108*, 5086.

[29] J. Zeller, J. Treptow, U. Radius, *Z. Anorg. Allg. Chem.* **2007**, *633*, 641.

[30] T. Kajiwara, S. Yokozawa, T. Ito, N. Iki, N. Morohashi, S. Miyano, *Chem. Lett.* **2001**, *30*, 6.

[31] N. Morohashi, N. Iki, S. Miyano, T. Kajiwara, T. Ito, *Chem. Lett.* **2001**, *30*, 66.

[32] H. Akdas, A. De Cian, E. Graf, J. M. Harrowfield, M. W. Hosseini, *Chem. Commun.* **2000**, 2219. (This concerns a tetracarboxylate derivative of the calixarene.).

[33] H. Katagiri, N. Morohashi, N. Iki, C. Kabuto, S. Miyano, *Dalton Trans.* **2003**, 723.

[34] W. B. Jennings, B. M. Farrell, J. F. Malone, *Acc. Chem. Res.* **2001**, *34*, 885.

[35] a) L. Pescatori, A. Arduini, A. Pochini, A. Secchi, C. Massera, F. Ugozzoli, *Org. Biomol. Chem.* **2009**, *7*, 3698 and references cited therein; b) D.-S. Guo, X. Su, Y. Liu, *Cryst. Growth Des.* **2008**, *8*, 3514.

[36] M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja, R. S. Burkhalter, *J. Am. Chem. Soc.* **1997**, *119*, 6324 and references cited therein.

[37] In work published while this manuscript was under review, the isolation of Ln_4OH species bound between a thiacalixarene sandwich has been extended to the cases of Tb and Dy. See: Y. Bi, X.-T. Wang, W. Liao, X. Wang, R. Deng, H. Zhang, S. Gao, *Inorg. Chem.* **2009**, *48*, 11743.

[38] N. Iki, K. Morohashi, C. Kabuto, S. Miyano, *Chem. Lett.* **1999**, *28*, 219.

[39] C. Floriani, R. Floriani-Moro in *Calixarenes 2001* (Eds.: Z. Asfari, V. Böhmer, J. M. Harrowfield, J. Vicens), Kluwer Academic Publishers, Dordrecht, **2001**, ch. 28, pp. 536ff.

[40] a) R. C. Mehrotra, A. Singh, *Prog. Inorg. Chem.* **1997**, *46*, 239; b) H. C. Aspinall, M. Williams, *Inorg. Chem.* **1996**, *35*, 255.

[41] E. J. Chan, B. G. Cox, J. M. Harrowfield, M. I. Ogden, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2004**, *357/8*, 2365.

[42] L. I. Semenova, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1996**, *49*, 997.

[43] G. M. Sheldrick, *SHELXL 97: A Program for Crystal Structure Refinement*, University of Göttingen, **1997**, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

Received: November 4, 2009