

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

## Abstract

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  $[(\mu\text{-H}_2\text{O})\{\text{Ln}(\text{O-dmf})_2\}_2(\text{HL-dmf})_2]\cdot n\text{S}$  (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  $\text{Ln}(\text{OH})_3\cdot 2\text{Ln}(\text{LH})\cdot x\text{dmf}\cdot y\text{H}_2\text{O}$  (2Ln, Ln = Yb, Lu), while both oxo and hydroxo species are isolable with Eu: trinuclear  $\text{Eu}_3\text{O}(\text{L})(\text{LH})_4\cdot 13\text{dmf}$  (3) and tetranuclear  $\text{Eu}_4\text{O}(\text{OH})_2(\text{L})(\text{LH}_2)_2(\text{LH}_4)\cdot 12\text{dmf}$  (9), both somewhat atypical species containing uncoordinated thiacalixarene molecules within the lattice. Anion ( $\text{NO}_3$ ,  $\text{ClO}_4$ ) 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<sub>3</sub> and Ln<sub>4</sub> aggregates are triangular or (quasi-)square-planar, except for  $\text{Gd}_4\text{O}_2(\text{LH}_2)_4\cdot 2\text{H}_2\text{O}\cdot 2\text{MeOH}\cdot 2\text{dmf}\cdot 3.375\text{CH}_2\text{Cl}_2$  (12), where there is a Z-disposition. Most common is an Ln<sub>3</sub>O core, which spans the gamut of Ln in three sets of crystal forms with cells of similar dimensions: for Ln = La...Nd,  $\text{Ln}_3(\text{OH})(\text{NO}_3)_4(\text{LH}_2)_2\cdot 4.5\text{dmf}$  (5Ln) (space group C2/m), and Sm...Lu,  $\text{Ln}_3\text{O}(\text{NO}_3)(\text{LH})_2\cdot 4\text{H}_2\text{O}\cdot 2\text{dmso}\cdot 2\text{MeCN}\cdot 3\text{py}$  (6Ln) (space group P21/n), conformity with crystallographic symmetry entails disorder of the Ln atoms; in a further form of lower symmetry Pn,  $(\text{pyH})\text{Ln}_3\text{O}(\text{NO}_3)_2(\text{LH})_2\cdot 2\text{MeCN}\cdot x\text{H}_2\text{O}\cdot y\text{dmso}\cdot 1.5\text{py}\cdot \text{MeOH}$  (7Ln, Ln = La, Ce), with no imposed crystallographic symmetry, some disorder persists, but none is found in the crystallographically unrelated form of 8Pr,  $\text{Pr}_3\text{O}(\text{NO}_3)(\text{LH})_2\cdot 16\text{H}_2\text{O}\cdot 2\text{MeCN}\cdot 5\text{py}$ .  $\text{Ln}_4(\text{OH})(\text{NO}_3)_3(\text{L})_2\cdot 8\text{dmf}\cdot 2\text{dmso}\cdot 3\text{H}_2\text{O}$  (10Ln, Ln = Pr...Gd, previously defined for Nd) has a square-planar Ln<sub>4</sub>O array sandwiched between a pair of L ligands, with a similar form found for  $\text{Ln}_4\text{O}(\text{ClO}_4)_2(\text{L}_2)\cdot x\text{dmf}\cdot y\text{H}_2\text{O}$  (11Ln, Ln = La...Nd).

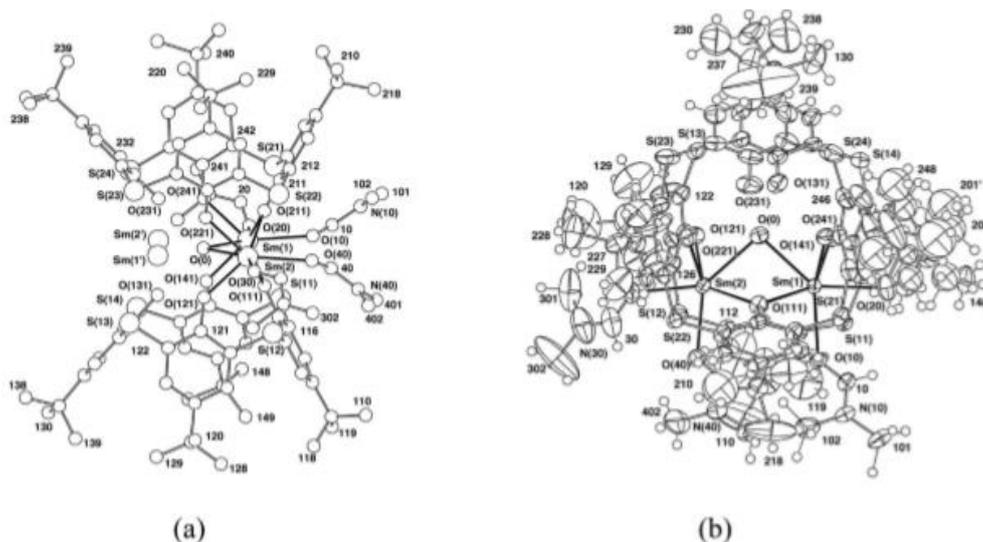


Figure 1. Projections of the binuclear array of  $[(\mu\text{-H}_2\text{O})\{\text{Sm}(\text{O-dmf})_2\}_2(\text{HL-dmf})_2]\cdot(2\text{dmf})$  (**1Sm**) (the molecule **1Eu** being similar, except that no core disorder is found): (a) The core, showing the location of the minor Sm components vis-à-vis 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.