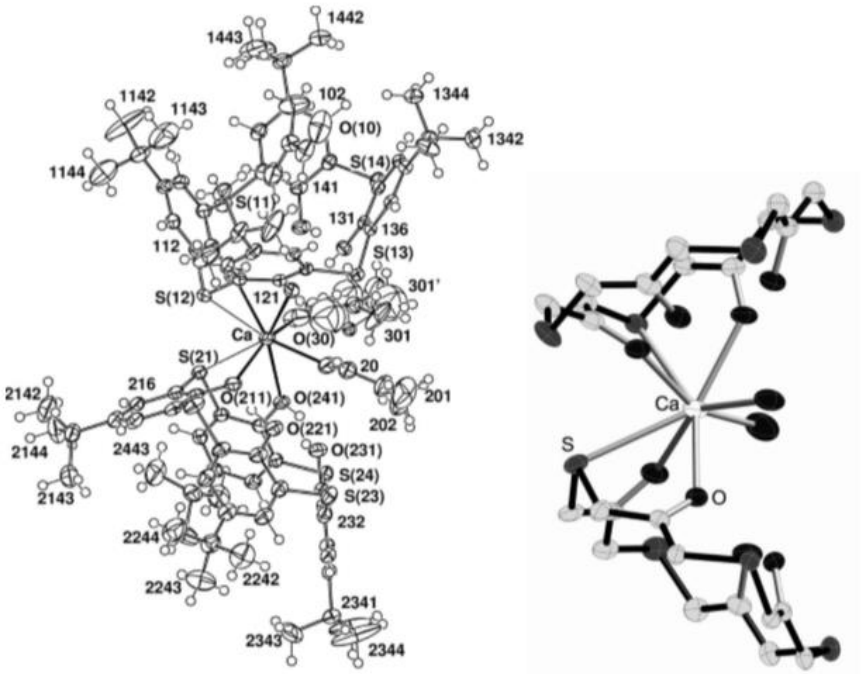
Systematic Structural Coordination Chemistry of p-tert-Butyltetrathiacalix[4]arene: Main Group Metal Complexes Other Than Those of Group

Abstract

In extension of previous work involving structural characterisation of complex salts formed between main group 1 metal ions and p-tert-butyltetrathiacalixarene, LH4, the present study encompasses complexes with a wider array of main group 2, 13, 14 metal ions. For group 2, single-crystal X-ray structural characterisation of Ca(LH3)2·3dmf (1a), {Ca(LH2)· 3dmf}2 (1b), Ba(LH3)2·6dmf (2a) and BaCO3·3Ba(LH3)2· 3H2O·3CH3CN·12.25CH2Cl2 (2b) provides models for various coordination units. For group 13, this applies to {Ga(OH)- (LH2)·3.5dmf}2 (3), {In(LH)·4EtOH·2CH2Cl2}2 (4a) and {In(OH)(LH2)·3CH2Cl2}4 (4b), and for group 14, to OPb4(LH)2· 6dmf·dmso·2H2O(5). Overall, these define mononuclear (1a, 2a), binuclear (1b, 3, 4b) and tetranuclear (2b, 4b, 5) species. The calixarene cavities frequently include solvent molecules, though this capacity is clearly influenced by the nature of the bound metal ion(s) and their binding, as well as the associated impact on the conformation of the calixarene ligand(s).



(a) (b)

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