

A mixed lithium–strontium polynuclear complex formed within the hexa-deprotonated calix[8]arene framework; the synthesis and structure of $\text{Li}_4\text{Sr}_2(\text{H}_2\text{L})(\text{O}_2\text{CC}_4\text{H}_9)_2(\text{dmf})_8$ [$\text{H}_8\text{L} = p\text{-Pr}^i$ - or $p\text{-Bu}^i$ -calix[8]arene] †

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The deprotonation of calix[8]arenes (H_8L) with Bu^nLi in DMF followed by reaction with dry SrBr_2 yielded the discrete molecular complexes $\text{Li}_4\text{Sr}_2(\text{H}_2\text{L})(\text{O}_2\text{CC}_4\text{H}_9)_2(\text{dmf})_8$ (H_8L : 1, $p\text{-Pr}^i$; 2, $p\text{-Bu}^i$); the crystal structures of these complexes of hexa-deprotonated calix[8]arenes show that mixed metal, polynuclear, inorganic cores can be formed within the large and flexible cavity of calix[8]arenes.

The binding of metal ions to the calixarenes and their derivatives is an area of intense research interest.¹ Although the coordination chemistry of the smaller calixarenes, and in particular the calix[4]arenes, has been investigated in great detail, the larger calixarenes potentially allow the formation of molecular, polynuclear complexes within their more flexible, central cavities. Several dinuclear complexes of the calix[8]arenes have been reported,^{1,2} but very few polynuclear complexes with three or more metal ions have been structurally characterised, and these are limited to two homotetranuclear examples with $p\text{-Bu}^i$ -calix[8]arene (H_8L): $\text{Th}_4(\text{HL})(\text{H}_2\text{L})(\text{OH})_3(\text{H}_2\text{O})_2(\text{dmsO})_4$,³ and $\text{Nb}_4\text{L}_2\text{O}_2\text{Cl}_8$.⁴ These are both sandwich structures with the polynuclear inorganic core formed between the two calixarenes. Sandwich structures are also found for the majority of the few homopolynuclear⁵ and heteropolynuclear⁶ complexes of calix[4]arenes ($\text{H}_4\text{L}'$) and thiacalix[4]arenes; the one exception being $\text{Li}_5\text{L}'(\text{OH})(\text{hmpa})_4$.^{5c}

As part of a study of the Group 1 and Group 2 coordination chemistry of the larger calixarenes,^{2a} we herein report the preparation and structure of the mixed metal, molecular, polynuclear calix[8]arene complexes of formula $\text{Li}_4\text{Sr}_2(\text{H}_2\text{L})(\text{O}_2\text{CC}_4\text{H}_9)_2(\text{dmf})_8$ [$\text{H}_8\text{L} = p\text{-Pr}^i$ -calix[8]arene for 1, $p\text{-Bu}^i$ -calix[8]arene for 2]. Polynuclear mixed Group 1 and Group 2 metal complexes containing four or more metal ions are uncommon,⁷ the majority being di- or tri-nuclear with straightforward structures.⁸ Surprisingly, no crystal structures of any mixed lithium–strontium complexes appear to have been reported,⁹ although the coordination chemistry of these metals with simple aryloxide ligands has been extensively investigated and both display a tendency to form polynuclear, molecular species.^{10,11} The calix[8]arene framework potentially provides eight aryloxide ligands convergent on the cavity within the macrocycle, thus the calix[8]arenes may be expected to favour the formation of such polynuclear complexes.

The reaction of H_8L (0.5 mmol) with eight equivalents of Bu^nLi in dmf (25 cm³) under argon formed a clear yellow solution that was transferred by cannula onto dry SrBr_2 (4 mmol). The solution was filtered to remove traces of

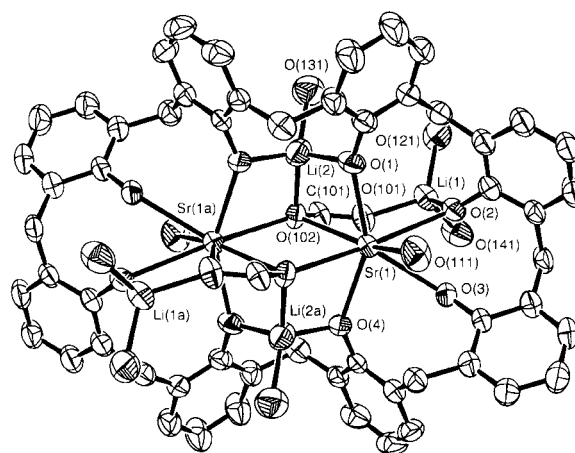


Fig. 1 ORTEP diagram for 1 (probability level 50%).¹⁴ For clarity only the oxygen atoms of the DMF molecules are shown, and the $p\text{-Pr}^i$ groups of the calix[8]arene, the Bu^n chain of the pentanoate ligand and all hydrogens have been omitted. Selected bond lengths (Å) and angles (°) for 1: Sr(1)–O(1) 2.441(4), Sr(1)–O(2) 2.828(4), Sr(1)–O(3) 2.672(4), Sr(1)–O(4) 2.447(4), Sr(1)–O(101) 2.496(4), Sr(1)–O(102) 2.671(4), Sr(1)–O(102a) 2.636(4), Sr(1)–O(111) 2.496(4), Li(1)–O(2) 1.943(11), Li(1)–O(101) 1.935(11), Li(1)–O(121) 1.967(12), Li(1)–O(141) 1.892(12), Li(2)–O(1) 1.876(11), Li(2)–O(4a) 1.786(12), Li(2)–O(102) 2.079(11), Li(2)–O(131) 1.960(13); Sr(1)–O(102)–Sr(1a) 106.79(13), O(102)–Sr(1)–O(102a) 73.21(13), Li(1)–O(2)–Sr(1) 96.7(3), Li(1)–O(101)–Sr(1) 102.4(3), Li(2)–O(1)–Sr(1) 96.8(4), Li(2)–O(102)–Sr(1) 85.3(3), Li(2)–O(4a)–Sr(1a) 106.7(4), Li(2)–O(102)–Sr(1a) 92.1(3); symmetry operation: a, $1 - x, 1 - y, 1 - z$.

insoluble by-products and a low yield (<5%) of X-ray quality crystals were obtained from the filtrate after 72 h. ‡ The presence of pentanoate in 1 and 2 is presumably due to the reaction of Bu^nLi with dmf to form pentanal, followed by adventitious oxidation.

The molecular structure of the lithium–strontium complex 1 is shown in Fig. 1; the structure of 2 is of lower quality but displays only small differences in bond distances and angles, and confirms the reproducibility of the formation of this core structure within the calix[8]arene framework. The structure of the polynuclear core formed within the hexa-deprotonated calix[8]arene of 1 is shown in Fig. 2. The complex has crystallographic inversion symmetry with a Sr(1)⋯Sr(1a) distance of 4.2606(10) Å and the strontium ion is eight coordinate with a distorted square antiprismatic geometry. All the calixarene oxygen atoms are coordinated to the strontium ions and the coordination sphere of each strontium is completed by a chelating pentanoate ligand, which also bridges the two strontium ions, and a terminal dmf molecule. The Sr–O(calixarene) distances cover the range 2.44–2.83 Å, broadly in line with the

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/suppdata/dt/1999/3535/>

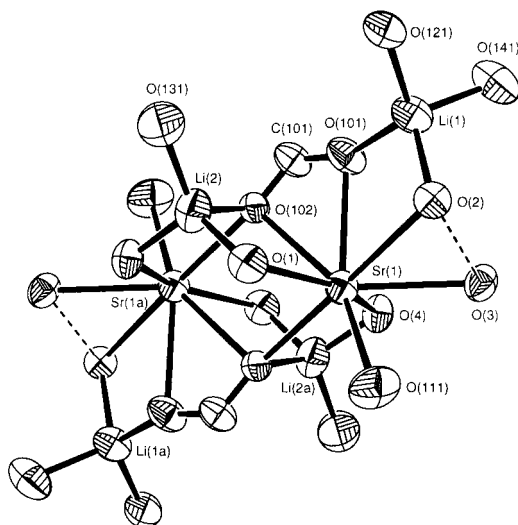


Fig. 2 ORTEP diagram for the polynuclear core of **1** (probability level 50%).¹⁴ The dashed lines highlight the short O(2)···O(3) distance of 2.440(5) Å, due to the strong intramolecular hydrogen-bonding of the two remaining calix[8]arene protons.

typical range of 2.40–2.76 Å for polynuclear complexes of monodentate aryloxides.¹¹ The two unique lithium ions both adopt distorted tetrahedral geometries: Li(1) is coordinated by two terminal dmf molecules and is doubly bridged to Sr(1) [through O(2) and O(101)] with a Li(1)···Sr(1) distance of 3.614(10) Å; Li(2) is coordinated by a single terminal dmf molecule and is doubly bridged to both Sr(1) [through O(1) and O(102)] and Sr(1a) [through O(4a) and O(102)], with Li(2)···Sr(1) and Li(2)···Sr(1a) distances of 3.249(11) and 3.418(12) Å respectively. Thus the pentanoate ligand bridges four metal ions and O(102) bridges Sr(1), Sr(1a) and Li(2) in the central Li₂Sr₂ face-sharing, bis-cuboidal core of the complex. Similar mixed-metal, bis-cuboidal core structures have been structurally characterised in the alkoxide complexes Li₂Sn₂(OBu)₆ and Li₂M₂(OPr)₁₀ (M = Ti, Hf).¹²

Charge balance requires that two calixarene protons remain in the complexes **1** and **2**, but these protons could not be located crystallographically. Previous work with partly deprotonated calix[8]arenes has shown that the remaining protons are found between pairs of calixarene oxygen atoms with characteristically short O···O distances.^{2a} Similar short hydrogen-bonding interactions of 2.489 and 2.504 Å have also been identified in monodentate aryloxide complexes of lithium and strontium respectively.^{10b,11b} Thus the very short distance of 2.440(5) Å between O(2) and O(3) strongly indicates the presence of a proton between these atoms (Fig. 2). This is also consistent with the observations for **1** that: (i) the Sr(1)–O(2) and Sr(1)–O(3) distances of 2.828(4) and 2.672(4) Å respectively are the longest in the Sr(1) coordination sphere despite the fact that O(3) is the only calixarene oxygen atom coordinated to a single metal ion, and (ii) the Li(1)–O(2) distance of 1.943(11) Å also appears somewhat lengthened.

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Notes and references

† Exact yields and elemental analyses could not be obtained due to the difficulty in isolating the low yield from the dmf solvent. *Crystal data*: Data for **1** and **2** were collected on the single crystal diffraction station (no. 9.8) at Daresbury Laboratory Synchrotron Radiation Source.^{5d,13} **1** C₁₁₄H₁₆₂Li₄N₈O₂₀Sr₂, *M_r* = 2167.52, triclinic, space group *P* $\bar{1}$, *a* = 13.079(2), *b* = 15.190(3), *c* = 16.187(3) Å, *α* = 76.844(5), *β* = 86.659(6), *γ* = 84.660(6)°, *U* = 3115.8(9) Å³, *T* = 160(2) K, *Z* = 1, *μ* = 0.919 mm⁻¹. 14144 reflections were measured, producing 8941 unique data with *R_{int}* = 0.0534, and 6827 unique data [*I* > 2σ(*I*)]. 724 parameters with 225 restraints refined to *R₁* = 0.0897 and *wR₂* = 0.2483

[*I* > 2σ(*I*)]. Notes on the refinement: positional disorder was modelled for one Pr³⁺ group, however the displacement parameters of its Ph group were not large enough to warrant the splitting of this group. The dmf molecule bonded to Sr(1) was refined as disordered over two sites. **2** C₁₂₂H₁₇₈Li₄N₈O₂₀Sr₂, *M_r* = 2279.72, triclinic, space group *P* $\bar{1}$, *a* = 13.3348(5), *b* = 15.2025(5), *c* = 18.5975(7) Å, *α* = 70.644(2), *β* = 73.347(2), *γ* = 79.079(2)°, *U* = 3389.2(2) Å³, *T* = 150(2) K, *Z* = 1, *μ* = 0.848 mm⁻¹. 10138 reflections were measured, producing 7730 unique data with *R_{int}* = 0.0372, and 5176 unique data [*I* > 2σ(*I*)]. 696 parameters with 298 restraints refined to *R₁* = 0.0961 and *wR₂* = 0.2661 [*I* > 2σ(*I*)]. Notes on the refinement: disorder was modelled for all Bu¹ groups. In two cases this involved a split site refinement of the carbon attached to the Ph ring, however the displacement parameters of the Ph groups were not large enough to warrant the splitting of these groups as well. One C atom, C(21), of a Bu¹ sidechain could not be located. CCDC 186/1644. See <http://www.rsc.org/suppdata/dt/1999/3535/> for crystallographic files in .cif format.

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