New structural motifs in lithium and zinc calix[4]arene chemistry†

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The structures of three novel compounds prepared from the reaction of the lower-rim 1,3-diacid calix[4]arene (LH₂) with lithium carbonate (1), *t*-butyl-lithium (2) and zinc acetate (3) are reported.

The versatility of calixarenes is now well documented with applications ranging from the encapsulation and delivery of anticancer complexes¹ to the extraction of radiotoxic elements from nuclear waste.² These uses stem from the facile functionalisation of either the lower or upper rims, and the conformational flexibility displayed by such ligands which often results in the beneficial presence of π -rich cavities. In the area of gas adsorption, early work by Atwood *et al.* revealed how sublimed *p*-*tert*-butylcalix[4]arene(OH)₄ ligand, shown to exhibit a bilayer structure with voids of *ca.* 235 Å³, was capable of absorbing N₂, O₂, CO, CO₂, and CH₄ with some degree of selectivity.³ More recently, studies were extended to acetylene together with a number of nitrogen oxides.⁴ Another member of the calixarene family, *p*-octanoylcalix[4]arene(OH)₄, was utilized by Ananchenko and Ripmeester *et al.* with adsorption isotherms measured for linear alkanes (C1–C4), ethylene, oxygen and nitrogen, at pressures of up to 4 bar and ambient temperature.⁵ In the case of hydrogen, for sublimed *p*-*tert*-butylcalix[4]arene(OH)₄ there was no observable up-take, a result which allows for H₂ purification in mixtures such as CO₂/H₂.⁶ However on increasing the H₂ pressure to 34.5 atm, an uptake of 0.2 wt% was recorded; similar values were noted for sublimed *p*-pentylcalix[4]arene(OH)₄ and *p*-octylcalix[4]arene(OH)₄.⁷

For some time, we have been interested in the coordination chemistry of calix[*n*]arenes.⁸ DFT calculations by Venkataramanan *et al.* suggested that lithium functionalised *p*-*tert*-butylcalix[4]arene(OH)₄ would possess significantly enhanced binding energy and would be capable of *ca.* 10 wt% H₂ uptake.⁹ With this in mind, we have embarked upon a programme of characterising, and screening for H₂-uptake, alkali-metal containing calixarenes. Herein, we present our findings using the ligand 25,27-bis(methoxycarboxylic acid)-26,28-dihydroxycalix[4]arene (LH₂) (Fig. 1).

Treatment of LH₂ with Li₂CO₃ in the presence of ZnCl₂ affords a pink complex [Li₂(calix[4]arene(OH)₂(OCH₂CO₂)₂]₃·*ca.* 3(EtOH) (1) which can be crystallised as hexagonal prisms† from ethanol in good yields (60%) by slow evaporation of the solvent. Although 1 turned out not to contain zinc, it was found that the presence of ZnCl₂ favoured crystallization. The calixarene units are linked *via* lithium carboxylate bridges (two per calixarene) into cyclic trimeric units (see Fig. 2), which, related by centres of symmetry, stack in such a way that alternate units are rotated 60° (Fig. 3) forming helical nanotubes, which pack in a 'honey-comb' arrangement (Fig. 4).¹⁰

These cylinders of trimeric units have an outer diameter of 20.36 Å (calculated from the distance between the three-fold symmetry axes through adjacent columns) and an internal diameter of 5.5 Å (calculated from the distance of the innermost non-hydrogen atom, Li(1), from the symmetry axis).

The pattern observed here is analogous to the structure of the crystallised ligand LH₂, as reported by Coleman and co-workers.¹¹ In that example, the self assembly of the

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†Electronic supplementary information (ESI) available: Synthetic details, X-ray powder diffraction, TGAs and crystal structure analysis of 1–3, including selected bond lengths and angles. CCDC 905210–905212. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32986g

Fig. 1 25,27-Bis(methoxycarboxylic acid)-26,28-dihydroxycalix[4]arene (LH₂).

Fig. 2 Diagram showing the cyclic arrangement of three calixarene units observed in **1**. Calix[4]arene units are linked about a three-fold symmetry axis which is parallel to the crystallographic *c* axis. The carboxylate groups (disordered, refined isotropically) shown are of one of several options for each group. Highly disordered solvent atoms in the central core have been omitted.

Fig. 3 Space-filling model of **1**, showing the stacking of trimeric units along the *c* axis. A small, lithium lined void is visible along the length of the resulting nanotube (Li = blue; second trimer = green).

supramolecules was attributed to the hydrophobicity of the calix[4]arene bis(methoxycarboxylic acid) bowl, compared to the hydrophilicity of the narrow rim substituents. Crystallisation of the calix[4]arene from methanol/water or chloroform/methanol gave helical nanotubes 20.6 Å in diameter (as defined above) with an internal channel of 6.9 Å in diameter (where the innermost non-hydrogen atom is O(16)). A similar structure was observed for the methyl ester of the calix[4]arene bis(methoxycarboxylic acid), which displayed a diameter of

Fig. 4 The hexagonal packing of individual nanotubes in the extended structure of **1**, when viewed in the *ab* plane.

19.0 Å with an internal channel of 5.5 Å (from corresponding calculations). In both these structures the formation of nanotubes is mediated by hydrogen bonding involving the carbonyl moieties of the pendant groups. It is of note that the ethyl ester of the calix[4]arene bis(methoxycarboxylic acid) did not follow this trend, but demonstrated the classical up/down packing frequently observed in the crystal structures of substituted calix[4]arenes.¹¹

This self-assembly of calix[4]arene supramolecules through hydrophobic–hydrophilic interactions has also been reported by Suwinska *et al.*¹² who showed that the hydrophobicity of the calix[4]arene bowl was increased by the presence of β -carbonyl-*para*-octyl groups on the upper rim of the calix[4]arene. The aggregation of the calix[4]arene units from non-anhydrous THF affords dodecameric ‘inverse micelles’ with a diameter of 42 Å and an internal void of 1100 Å³ which contained disordered water molecules. The close proximity (4.6 Å) of the ‘micelles’ allows for the entanglement of the β -carbonyl-*para*-octyl groups between neighbours that gave rise to a second smaller pore of 130 Å³. Diffuse electron density in these voids suggests that water molecules are also present here. Many other examples of amphiphilic calix[4]arene structures exist in the literature, however there are very few examples of these structures being mediated by the presence of metal ions. One such example was reported by Orr.¹³ The self assembly of spherical and tubular structures here has been achieved through the reaction of the pentasodium salt of *p*-sulfonatocalix[4]arene with La(NO₃)₃·6H₂O and *N*-pyridine oxide, with the morphology of the resultant nanoarchitecture being controlled through the variation of the molar ratios of reactants. The structure reported herein, however, is the first example of a calix[4]arene diacid being linked *via* lithium–carboxylate bonds to form helical nanotubes.

In an attempt to achieve a greater degree of lithiation at the lower rim of LH₂, the ligand was reacted with *t*BuLi in THF under anhydrous conditions, followed by crystallisation from dry ethanol. The involvement of the hydroxyl functions of the calix[4]arene dimethoxycarboxylic acid led to the formation of a dimeric structure, [Li₂(calix[4]arene(OH)₂(OCH₂–

Fig. 5 ORTEP diagram showing the lithium-calix[4]arene dimer, complex **2**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except those involved in hydrogen bonding) are omitted for clarity.

Fig. 6 ORTEP diagram showing the chains resulting from intermolecular hydrogen bonding between the dimer units in complex **2**.

$\text{CO}_2)_2(\text{EtOH})_2$ **2**, again with each calixarene bound to two lithium ions (Fig. 5).[†] In this case however, one of the lithium atoms is bound to an ethanol molecule, which provides an OH group for intermolecular hydrogen bonding with an acid group of the neighbouring dimer, giving infinite chains (Fig. 6).

The reaction of LH_2 with zinc acetate under solvothermal conditions yields the coordination polymer $[\text{Zn}(\text{calix}[4]\text{arene}(\text{OH})_2(\text{OCH}_2\text{CO}_2)_2(\text{DMF})(\text{H}_2\text{O}))_n$ (**3**) (Fig. 7).[†] In this example, each metal centre is bound to three calix[4]arene units (*via* acid moieties), a DMF and a water molecule, the latter molecules binding in equatorial positions giving pseudo-trigonal bipyramidal zinc centres. The carboxylate unit of O(313) and O(314) bridges two metal centres giving infinite chains through the crystal, parallel to the *a* axis. These chains pack in an offset herringbone pattern with the coordinated DMF molecule dipping into the cavity of the neighbouring calix[4]arene unit. No intermolecular binding is observed between the chains.

Thermogravimetric analyses (TGA) of **1**, **2** and **3** were performed under an inert carrier flow (He) to further elucidate their solid-state stabilities. The TGA traces are compared in

Fig. 7 Zinc(calix[4]diacid) chains of complex **3**, viewed down the *b* axis.

Fig. 8 Recorded TGA traces for complexes **1**, **2** and **3**.

Fig. 8 and reveal similar profiles at lower temperature. Neither the channel material, **1**, nor the chain polymer, **3**, showed any appreciable mass loss between 25–240 °C that could be ascribed to loss of solvent from pore regions within the lattices. Instead, the onset of continuous structural decomposition was observed in both cases above 250 °C. In the case of **3** this is expected, as the tight packing of the chains prevents the inclusion of unbound solvent molecules. In the case of complex **1**, however, diffuse electron density suggests the presence of solvent molecules in the lithium lined pores.

Complex **2** underwent a localized 12% mass loss in the range 150–230 °C and was then stable up to 290 °C. This mass loss may be ascribed to the loss of two unbound ethanol and four water molecules per dimer unit. Above 600 °C and even at 800 °C, **3** maintained 52% total mass. In comparison, major degradation was observed in the Li(I)-containing **1** and **2** that both showed almost complete combustion at 800 °C. This makes sense, since presumably above 800 °C, the Zn will most likely be present in the oxide form, in addition to other carbonaceous species derived from the ligands (*e.g.* graphitic carbon). Similarly, for **1** and **2** above 800 °C, there will be

nothing left of the materials in terms of their structural integrity (the carrier gas employed was UHP He).

Gas adsorption isotherms were collected for complexes 1–3 after activation of crystalline samples under vacuum (10^{-10} bar) at 150 °C for 4 h, using various probe adsorbates (H_2 , 78 K; N_2 , 78 K; CO_2 , 196 K). Unfortunately, the materials did not show appreciable uptake of any of these molecules, as predicted by the lack of desolvation from the TGA experiments.

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Notes and references

†Crystal data for compound 1: $\{\text{C}_{32}\text{H}_{26}\text{Li}_2\text{O}_8(\text{ethanol})\}_3$, $M = 1657.2$. Trigonal, space group $R\bar{3}$ (no. 148), $a = b = 35.2552(11)$, $c = 11.7244(3)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 12\,620.2(6)$ Å³. $Z = 6$, $D_c = 1.308$ g cm⁻³, $F(000) = 5184$, $T = 140(1)$ K, $\mu(\text{Mo-K}\alpha) = 0.9$ cm⁻¹, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $\theta_{\text{max}} = 23^\circ$, $R_1 [I > 2\sigma(I)] = 0.057$, wR_2 (all data) = 0.170.

Crystal data for compound 2: $(\text{C}_{32}\text{H}_{26}\text{Li}_2\text{O}_8, \text{C}_2\text{H}_6\text{O})_2$, $M_r = 1196.96$. Triclinic, space group $P\bar{1}$, $a = 10.3639(7)$, $b = 11.7721(5)$, $c = 11.8355(8)$ Å, $\alpha = 87.429(4)^\circ$, $\beta = 78.483(3)^\circ$, $\gamma = 83.793(4)^\circ$, $V = 1406.22(15)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.413$ Mg m⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71073$, $T = 120(2)$ K, $\theta_{\text{max}} = 22.5^\circ$, $R_1 [I > 2\sigma(I)] = 0.079$, wR_2 (all data) = 0.192.

Crystal data for compound 3: $\text{C}_{32}\text{H}_{27}\text{O}_8\text{Zn}_2\text{OH}_2\text{C}_3\text{H}_7\text{NO}$, $M_r = 695.01$. Orthorhombic, space group $P2_12_12_1$, $a = 9.9928(5)$, $b = 17.3371(11)$, $c = 17.7642(9)$, $V = 3077.6(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.500$ Mg m⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71073$, $T = 140(1)$ K, $\theta_{\text{max}} = 25^\circ$, $R_1 [I > 2\sigma(I)] = 0.076$, wR_2 (all data) = 0.127.

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