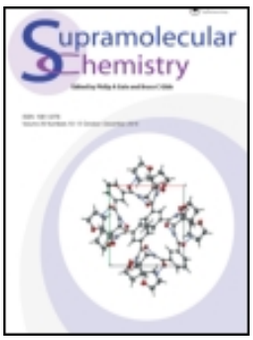

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Pb, Sr and Ba calix[6]arene hexacarboxylic acid octahedral complexation: a dramatic effect of dealkylation

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Calix[6]arene hexacarboxylic acid binds instantly and with low symmetry to Pb, Sr and Ba. Later a highly symmetric up-down alternating conformation emerges. The solution structures are identical to their p-tert-butylcalix[6]arene hexacarboxylic acid counterparts. With either receptor, an octahedral cage is formed around the metal. The transformation from low to high symmetry however proceeds at significantly faster rates for the de-t-butylated host.

Keywords: word; another word; lower case except names

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Introduction

t-Butyl calix[6]arene hexaesters and hexaamides have enhanced selectivity towards the extraction and transport of a variety of ions including Cs(I) and Sr(II) (*1–5*). Pb(II) is effectively transported by the hexaester (*6,7*). t-Butyl calix[6]arene hexathioamides (*8*) have been shown to be efficient towards Cu(II) (*9*), Pb(II) (*7*) and Ag(I) (*10*). Variation in selectivity changed when several of these compounds lacked p-tert-butyl groups – and in many cases binding affinity was drastically enhanced (*11,12*). Calix[n]arene phosphine oxides (*13*) have also demonstrated enhanced binding affinity for Th(IV) (*14*). Indeed, work with calix[6]arenes towards nuclear waste separation remains an ongoing area of active research (*15*).

Very recently, we reported on the complexation of Pb(II), Sr(II) and Ba(II) with p-tert-butylcalix[6]arene hexacarboxylic acid **1** (Figure 1) (*16,17*). In these reports, we found that calixarene hexacarboxylic acid binds rapidly with all three metals and form low-symmetry 'lozenge' shaped complexes (*18*). These exhibit complex NMR signals with multiple types of methylene bridges for both the ether as well as the aryl linkages. Upon standing something remarkable occurred – all three metal–host complexes rearrange such that the individual phenyl rings alternate up-down so that the carboxylates form an octahedral cage with C_{3V} symmetry around the metal centre. NMR and X-ray measurements for all three complexes confirm the solution and solid-state structure of the host. The structures we reported have some semblance to valinomycin·K (*19*) or Cram's sphereands (*20*). With these metals – differences in time to rearrange were apparent. We demonstrated that several analogues of calixarene hexacarboxylic acid, such as those where acid was replaced with ether, di-ether or ester, resulted in initial low-symmetry binding, but only those hosts with acid functional groups resulted in an octahedral cage for the metal. This behaviour was attenuated when amine bases were added, presumably due to ion capping (*21*). The use of other bases to date has not had a marked impact on the behaviour of these host–guest complexes, although our studies have not been exhaustive. A variety of other metals were tested and Pb, Sr and Ba are a short list of metals that this host is selective for accommodation in an octahedral environment.

The remaining variable of interest to us was the effect of the t-butyl group (*22*). Is it possible that the t-butyl group has an influence on either binding or the rate of conversion from a low- to high-symmetry complex for these three metals?

Results and discussion

Calix[6]arene hexacarboxylic acid **2** is a known compound (*21*). We prepared **2** through removal of *tert*-butyl group of *p-tert*-butylcalix[6]arene by adopting a procedure reported for p-tert-butylcalix[4]arene (*23*). Alkylation and sapponification as for **1** (*16*) gave **2** (Figure 2).

When **2** was mixed with 1 equivalent of $Pb(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ immediate formation of one major species was obvious (Figure 3), but some very small peaks that can be attributed to low-symmetry 'lozenge' shaped species co-exist. After 30 min however the sample appears to be at equilibrium with a high-symmetry geometry that is identical in pattern to the analogous p-tert-butyl host (Figure 4) (*16*). The complex remains soluble in a mixture chloroform/acetonitrile and is highly

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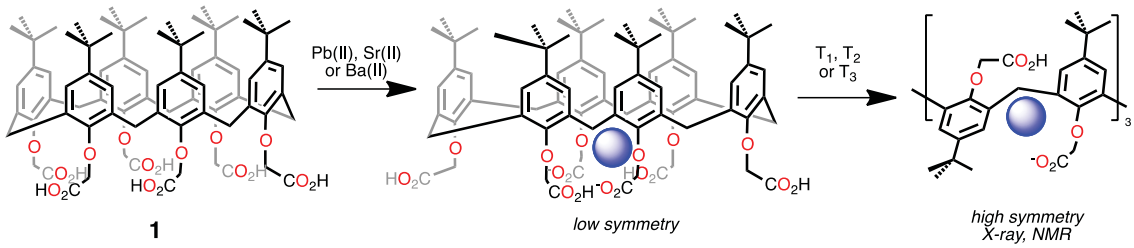

Figure 1. (Colour online) *p*-tert-Butyl calix[6]arene hexacarboxylic acid **1**; its low-symmetry 'lozenge' solution structure with Pb, Sr and Ba; and a truncated solution (and solid state) structure after adopting a high-symmetry C_{3V} conformation (based on NMR and **3** X-ray structures).

likely to be neutral. The exact location of all protons isn't known, but we surmise that 2 negative charges and 4 protons are distributed amongst the 6 carboxylates and are interchanging – indeed the symmetry of the solution-state structure supports this assumption as well as exact mass measurements (see ESI).The two sets of diastereotopic methylenes are split drastically. For the bridging methylene, this isn't surprising; in a cone conformation calix[n]arenes place one H 'down' and the other 'out'. In our alternating up-down conformation, this relationship remains. The second methylene group, a phenolic ether also undergoes drastic splitting; for **1**·Pb (*16*) this result was explained with NOESY and X-ray data, one hydrogen points towards an adjacent aromatic proton, the other

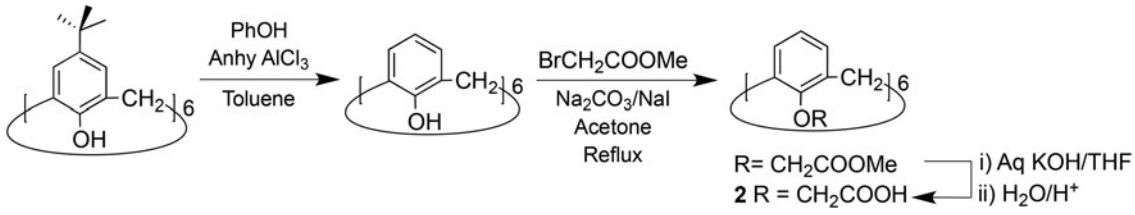

Figure 2. Preparation of calix[6]arene hexacarboxylic acid **2**.

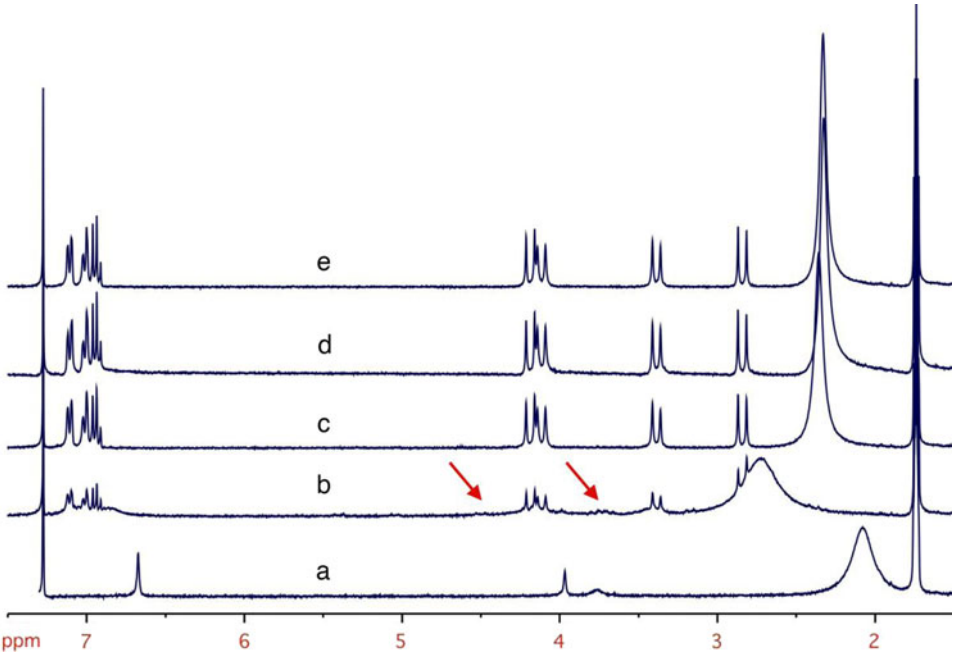

Figure 3. (Colour online) H-NMR (400 MHz) of 2.5 mM**2** in presence of 1 eq$Pb(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1:1). From bottom to top: ligand **2**(a), at the time of mixing with Pb (b), after 30 min (c), after 1 h (d), and 4 h (e), respectively The NMR signals are with reference to residual CH_3CN signal at 1.94 ppm. Red arrows show faint traces of low-symmetry 'lozenge' conformation.

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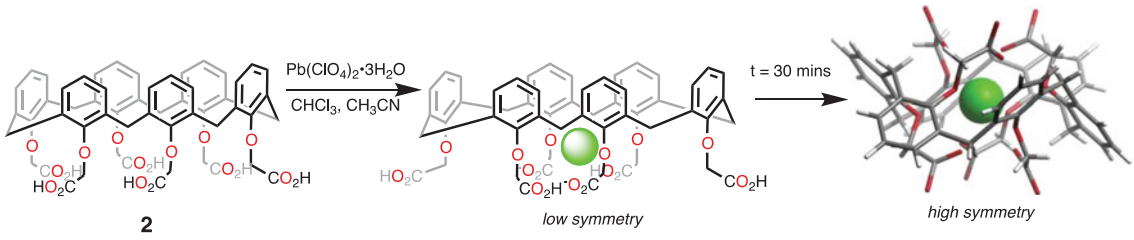

Figure 4. (Colour online) Conformational reorganisation of **2** when mixed with Pb(II) with rendered model (MMFF) based on NMR data comparison to **1·Pb**, some protons omitted for clarity.

away. The same is now true for **2**·Pb(II) (see ESI for COSY, NOESY, HSQC spectra). In the instance of **2**, however, the transformation is complete in 30 min; previously with the more hindered host **1**, the transformation takes approximately 15 h.

Given the drastic reduction in time for the formation of the octahedral complex of **2**·Pb (1 h) vs. **1**·Pb (15 h), we anticipated that the rearrangement of **2**·Sr would also proceed more quickly than its t-butyl analogue **1**·Sr. **1**·Sr took approximately 20 days to come to equilibrium. Sr $(ClO_4)_2{\cdot}3H_2O$ was again slow to entice host **2** into octahedral geometry, upon mixing several low-concentration species are present (Figure 5) and several major broad peaks emerge. From 48 h to 72 h (latter not shown), the signals remain poorly resolved and broad, but at 115 h baseline resolution is achieved and we ascribe this to be an approximate time to arrive at equilibrium. A small peak at 7.0 ppm remains that is part of the free ligand **2**.

Finally, we conducted the same experiment with Ba $(ClO_4)_2{\cdot}3H_2O$. Many sharp signals exist for **2**·Ba at the time of mixing, consistent with a low-symmetry lozenge (Figure 6). At 48 h after mixing, the sample is at equilibrium. This last result is most surprising because the high-symmetry **1**·Ba sample took 38 days of time to come to equilibrium, both Pb and Sr were faster with host **1**. These results are summarised in Table 1 and we see that the t-butyl group of **1** has a marked effect on the time it takes complex **1** vs. **2** to arrive at equilibrium. In all cases, equilibrium is arrived at an order of magnitude sooner. Surprisingly though, the behaviour is not consistent – Ba

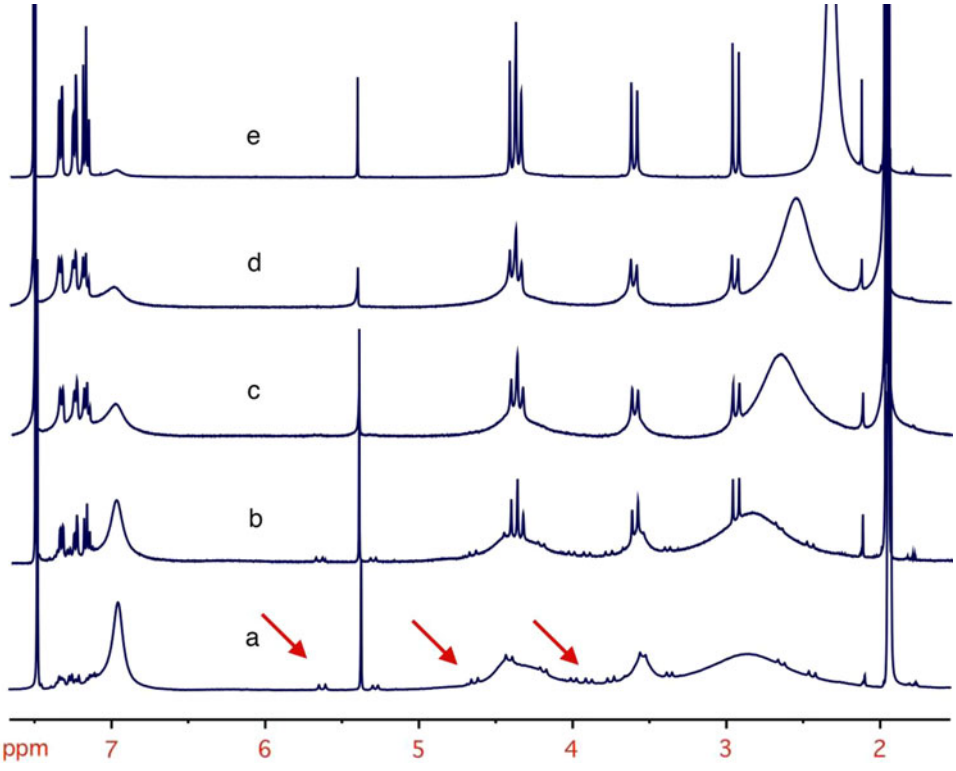

Figure 5. (Colour online) H-NMR (400 MHz) of 2.5 m**M2** in presence of 1 eqSr$(ClO_4)_2{\cdot}3H_2O$ in $CDCl_3/CD_3CN$ (1:1). From bottom to top: at the time of mixing with Sr (a), after 8 h (b), after 30 h (c), after 48 h (d), and after 115 h (e), respectively. The NMR signals are with reference to residual CH_3CN signal at 1.94 ppm. Red arrows show evidence of low-symmetry 'lozenge' conformation.

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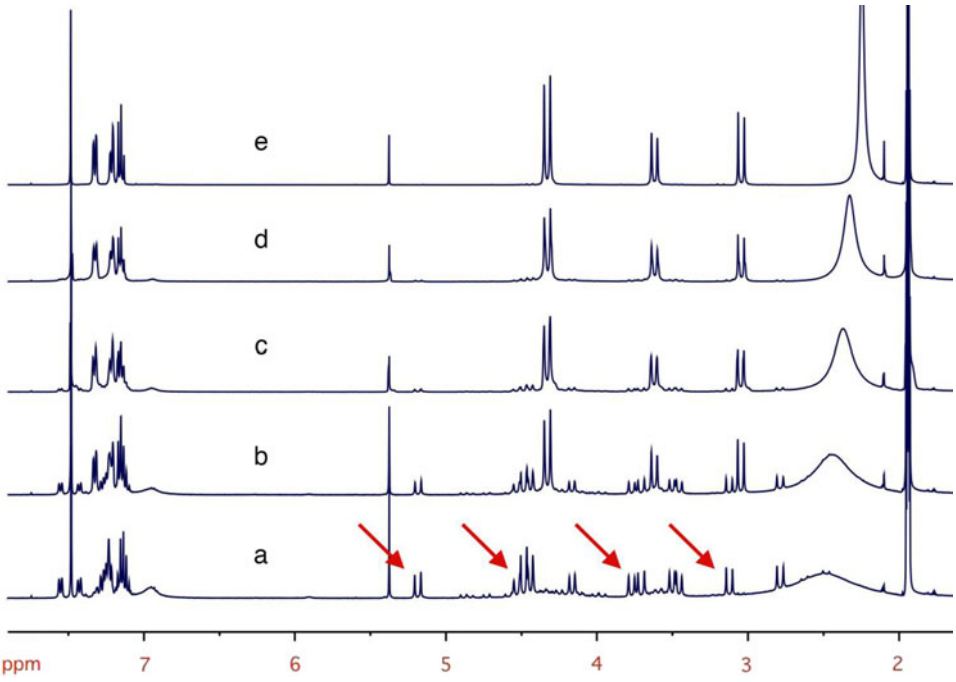

Figure 6. (Colour online) H-NMR (400 MHz) of 2.5 m**2** in presence of 1 eq$Ba(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1:1). From bottom to top: at the time of mixing (a), and after 8 h (b), 20 h (c), 30 h (d), and 48 h (e), respectively. The NMR signals are with reference to residual CH_3CN signal at 1.94 ppm. Red arrows show some of the many peaks of low-symmetry 'lozenge' conformation.

and Sr switch their ranking as a function of host, always slower than Pb. It remains unclear why Ba and Sr don't have the same relative order of time to reach equilibrium.

We added 10% v/v of D_2O to test the stability of the complex and found that they rapidly degraded. First observations of NMR show a series of broadened peaks that promptly disappear (see ESI). No evidence of NMR signals could be found when **2** was directly mixed with Pb, Sr or Ba in pure water.

Given the drastic change in the time it takes host **2** to rearrange, we conducted an initial screening programme to uncover other metals that might be accommodated in this octahedral hole. As was the case with **1**, **2** fails to show evidence of complex formation with Ca(II), Y(III), Bi(III) or Gd(III) (see ESI for details). While new complexes weren't found, it is clear that **2** remains a selective host.

Given the time differences to arrive at equilibrium, we conducted a competitive binding experiment using a 1:1:1 ratio of **1**, **2** and Pb(II) (Figure 7). At the initial time of mixing, the **2**·Pb complex is easily identified as the predominant complex. Traces of **1**·Pb and the low-symmetry complex of **1**·Pb can be identified. At the 16 h mark, the two high-symmetry complexes are present and the t-butyl **1**·Pb host is the major component. Surprisingly after 115 h evidence of a roughly 1:1 mixture of **1**·Pb:**2**·Pb was apparent. Complex **2**·Pb more quickly converts from low to high symmetry; the dynamics of the system remain under investigation. Perhaps solubility differences are at work after more than 16 h of resting while the system reverts to 1:1.

Next, we performed a competitive binding experiment between host **2**, Pb and Ba. Mixing the three components in a 1:1:1 molar ratio, we see rapid formation of the high-symmetry Pb complex after 4 h – the Pb complex is readily identified. After 115 h, the Ba complex surpasses the concentration of Pb (Figure 8).

Host **1** and **2** now both serve as calix[6]arene hosts that display a remarkable conformational change when binding with Pb, Sr and Ba. In all combinations – initial low-symmetry species are identified by NMR and given enough time high-symmetry octahedral complexes are formed. These complexes display a unique alternating up-down arrangement of calix[6]arene phenyl groups so as to surround the metal centre with 6 carboxylate groups. We have clearly demonstrated the effect of removing the t-butyl groups of **1**; by using **2** the time to reorganisation decreases by an order of magnitude (from weeks to days, or 15 h to 30 min). The relative rates to equilibrium however change with differential behaviour for Sr and Ba

Table 1. Times to arrive at high-symmetry octahedral coordination for hosts **1** and **2** with Pb, Sr and Ba. All species at 2.5 mM in $CDCl_3/CD_3CN$ (1:1).

	Host **1**	Host **2**
Pb(II)	15 h	30 min
Sr(II)	20 days	115 h
Ba(II)	38 days	48 h

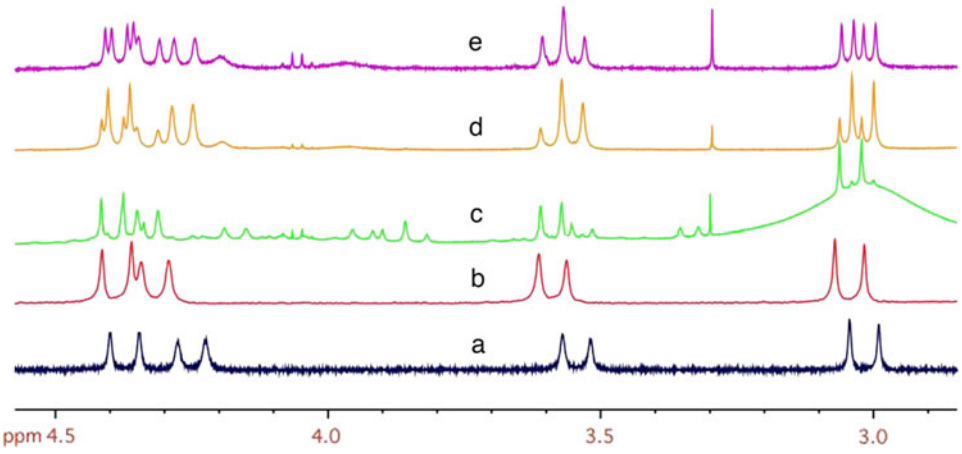

Figure 7. (Colour online) ^{1}H-NMR (400 MHz, in $CDCl_3/CD_3CN$). Expanded stack plot from bottom to top: **1**·Pb (a), **2**·Pb (b), an initially mixed sample of 5 mM of **1** + **2** + Pb (1:1:1) (c), the mixed sample after 16 h (d), and 115 h (e).

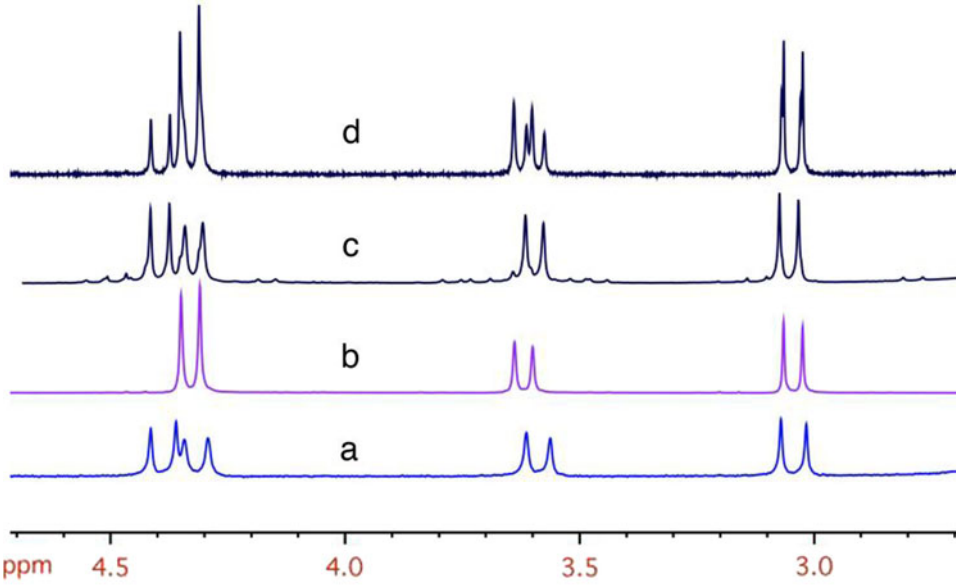

Figure 8. (Colour online) ^{1}H-NMR (400 MHz, in $CDCl_3/CD_3CN$). Expanded stack plot from bottom to top: (a) **2**·Pb, (b) **2**·Ba, (c) a sample of **2** + Pb + Ba (1:1:1) after 4 h, and (d) after115 h.

with **1** and **2**. Additionally, initial competitive binding experiments reveal some new details about stability and dynamics. Other combinations are currently being explored to thoroughly evaluate the competitive binding affinity and kinetics of Pb, Sr and Ba for both hosts **1** and **2**. At the end of these studies, we hope to develop materials suitable for deployment towards the separation of Pb or Sr from complex waste streams.

Experimental

All spectra described above are provided in the ESI along with complete characterisation of all new compounds, some experimental procedures are cited above.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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