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# p-tert-Butylcalix[6]arene hexacarboxylic acid as host for Pb(II), Sr(II) and Ba(II)

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p-tert-Butylcalixarene hexacarboxylic acid initially binds with low symmetry, to later adopt a highly symmetric up-down alternating conformation in the presence of Pb, Sr or Ba. The conformational dynamics for the three ions are distinct, from 15 hours, to 20 days, to 38 days, respectively.

## Introduction

Calix[n]arenes are macrocyclic compounds able to form host-guest inclusion complexes with metal ions,[1] small organic molecules and small moieties of larger molecules.[2-5] Recently we demonstrated that a variety of upper and lower functionalized calixarenes can transport choline appended fluorophores across liquid membranes based on anion-trimethyl ammonium recognition.[6] When modified with proper ligating sites the lower rim can provide a preorganized vase shape that binds small, cationic guests such as metals.[7, 8] Calixarenes with various substituents at lower rim have shown their preferential binding of one over another cation due to size effect as well as due to selectivity effect of the functional group.[9-11] Consequently, a number of compounds have been developed that enjoy considerable utility in analytical chemistry such as the sensing of toxic cations.[12, 13] In engineering applications the separation of radionuclides exploits these same ideas.[14-18] Moreover, calixarenes are enjoying success in catalysis when bound to metals such as Al and Ti.[19, 20]

Although the calixarene literature regarding metal ion complexation with calix[4]arene derivatives is extensive, only a few reports deal with metal ion binding events of conformationally labile larger calixarenes.[21] When suitably functionalized, the larger and conformationally flexible calixarenes can form strong inclusion complexes with larger cations[22] and a calix[6]arene hexaester can affect transport of Pb.[23] In these binding instances, the metal ion acts as a template to induce structural reorganization of the ligand. In some cases, a positive cooperative effect between the two metal ion binding sites is often observed.[14]

Very recently we found that the initial low-symmetric, lozenge-structure of calix[6]arene hexacarboxylic acid complexes with Pb(II) and undergoes a remarkable conformational reorganization.[24] After 15 hours, the carboxylates present an up-down alternating configuration, presenting a highly-symmetric octahedral coordination environment to an entrapped Pb. We observed similar, albeit slower solution phase conformational changes for Sr(II) and Ba(II).

Herein we report on our complete solution and solid-state findings for Sr and Ba. Additionally we examine the role that amine bases play in the complexation and conformational changes associated with carboxylic acid functionalized calix[5]- and [6]arenes and systematically explore the role of acid with a comparison against ester and ether functional groups.

## Results and discussion

Calix[5]arenes **1a-1f** and calix[6]arenes **2a-2f** were prepared following known methods[25] from the corresponding t-butylcalix[5]arene (**1**) and t-butylcalix[6]arene (**2**) (Figure 1). Calix[6]arene hexacarboxylic acid **2d** is central to our discussion and the other compounds will serve to illustrate the unique features of **2d**.

### Sr(II) and Ba(II) slowly form an octahedral cage with 2d

With Pb(II) we found that **2d** forms a low symmetry "lozenge shaped" complex within 3 minutes of mixing (the time required to acquire a spectrum) and after 15 hours there was solution and solid state evidence indicative of a drastic conformational change. The result was a high-symmetry octrahedral complex with up-down alternating phenyl units, placing the carboxylates at the six corners of an octahedron. Pb(II) fits perfectly in this nook.[24] Sr(II) however behaved differently. The initially formed low symmetry complex emerges upon mixing (Figure 2, and ESI) and shortly thereafter many species co-exist. After

7 days the solution is nearly at equilibrium with one predominant high symmetry arrangement – fully consistent with the solution structure of the **2d**•Pb(II) complex. The aromatic protons, as well as the phenolic methylene unit become diastereotopic due to a rigid "up-down" alternating arrangement of phenyl rings. This has previously been confirmed with x-ray and 2D NMR.

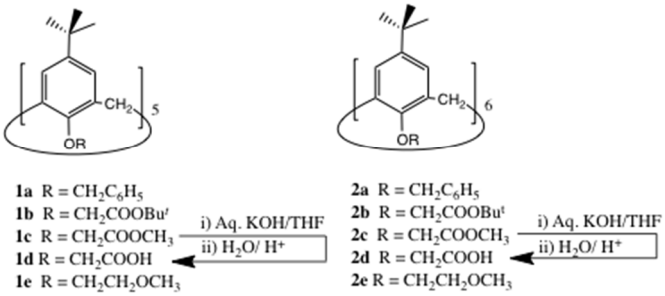


Figure 1. Molecular structures of calix[5] and calix[6] arenes used in this report.

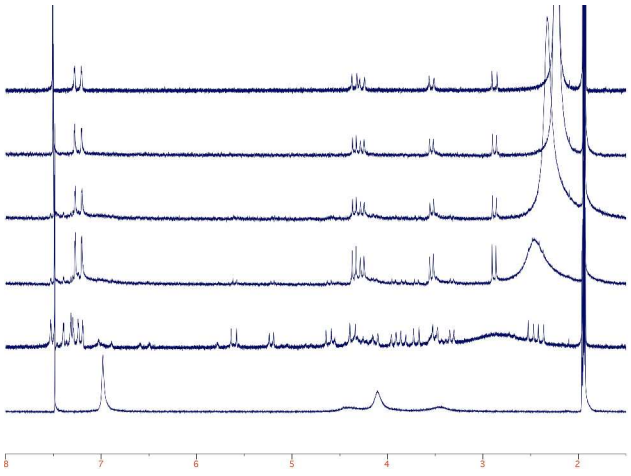

Figure 2. $^1$H NMR (400 MHz) Time dependent binding of **2d** with Sr(II) in $CDCl_3/CD_3CN$ (1:1). From bottom to top: Free ligand **2d**, **2d** + 1 eq Sr(II), **2d**+ 1eq Sr(II) after 7 days, 12 days, 20 days and 30 days. NMR signals are with reference to $CD_3CN$ at 1.94 ppm. The sharp signal at 7.49 ppm is due to $CDCl_3$ and the broad signal at around 2.5 ppm which intensifies with time is due to $H_2O$ from $Sr(ClO_4)_2•3H_2O$.

With Ba(II) and **2d**, the initial NMR pattern is very different from that of its Pb(II) and Sr(II) counterparts (Figure 3 and ESI). The symmetry of the NMR is higher than that of the "lozenge" but at this time we cannot ascertain much more. What is clear is that **2d** can adopt different geometries to accommodate cations inside the cavity formed by coordinating atoms, it is likely that the observed behavior is attributable to the differences in size or hardness of these cations. In this instance, Ba(II) *very slowly* entices the calixarene host into a octahedral coordination arrangements – giving rise to a solution structure similar to those of Pb and Sr, but taking 38 days. Characteristic aromatic protons and methylene units emerge from 3 to 4.5 ppm.

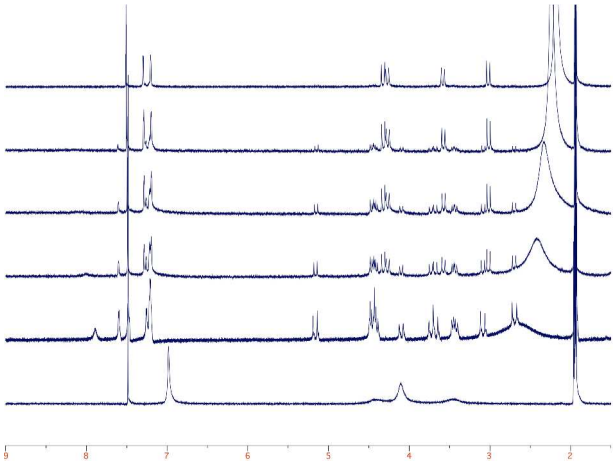

Figure 3. $^1$H NMR (400 MHz) Time dependent binding of **2d** with Ba(II) in CDCl3/CD3CN (1:1). From bottom to top: Free ligand **2d**, **2d** + 1 eq Ba(II), **2d**+ 1eq Sr(II) after 7 days, 12 days, 20 days and 38 days. NMR signals are with reference to CD3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to CDCl3 and the broad signal at around 2.5 ppm which intensifies with time is due to H2O from $Ba(ClO_4)_2•3H_2O$.

**Solid state evidence for octahedral coordination of 2d with Sr(II) and Ba(II)**

We reported on the solid state structure of **2d**•Pb(II) previously.[24] Additionally, a diethylamide analog of **2d** has previously been shown to coordinate with Sr(II) in a low symmetry arrangement where 4 of the 6 lower rim amides form a cage around Sr with both ether and carbonyl groups poised appropriately.[26] The remaining 2 amide groups sit vacant nearby. Slow evaporation of an equilibrium sample of **2d**•Sr(II) gave single crystals with near identical parameters for our **2d**•Pb(II)complex.

With **2d**•Sr(II) we find that a drastic conformational change has occurred, the vase (when uncomplexed) and lozenge (when initially complexed) shapes in solution (Fig. 2) are gone and replaced with a remarkable alternating arrangement of up-down phenyl units (Figure 4). This structure is consistent with the equilibrium state observed by NMR after 12 days. The structural reorganization is similar to valinomycin•K[27] and bears similarity to Cram's preorganized spherand.[28]

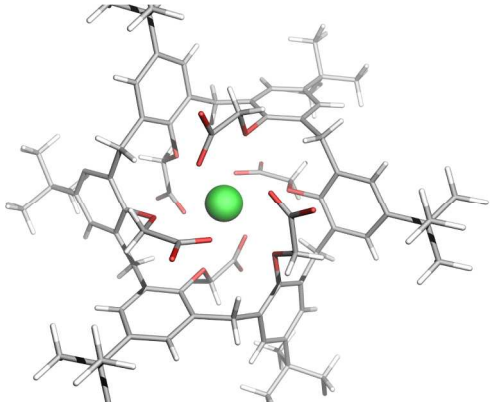

Figure 4. Rendered x-ray crystal structure of equilibrium **2d**•Sr(II) host•guest complex.

Single crystals of **2d**•Ba(II) complex with suitable size for single crystal X-ray diffraction analysis were not found. Nevertheless, a poly crystalline powder sample was isolated at equilibrium (as determined by NMR after 38 days) after evaporation. This material proved suitable for powder X-ray diffraction analysis. TREOR methods were used to index the peaks and all the peaks were indexed based on a cubic unit cell with $a$ = 28.499(4) Å. This result is consistent with what was obtained from single crystal data for **2d**•Pb(II) with a = 28.3035(7) Å and **2d**•Sr(II) with a = 28.3335(7) Å. The slight increase in cell dimensions of the unit cell is due to the larger ionic radius of Ba(II) compared to that of Sr(II) (See ESI for more details).

**Effects of base on Pb(II) complex formation with 2d**

We were curious about the role of charge with respect to the rate of complex formation and conformational switching. We chose to use Pb(II) for these studies due to its shorter time to reach equilibrium with **2d**. We prepared a sample of **2d** with 2 molar equivalents of triethylamine (Figure 5). The signals from triethylamine were downfield shifted and a slight upfield shift was observed for the H NMR signals of the methylene closest to the carboxylates in **2d**, these observations are consistent with a change in protonation state for both species. In presence of 6 equivalents of triethylamine, a cone conformation of **2d** was still evident. We had hoped that deprotonation of carboxylates would accelerate binding and or switching, but this was not the case – upon addition of Pb(II) there was a decrease in the amplitude of the signals for **2d** and no new peaks emerged. This is likely due to ion-pair capping of hexacarboxylate anions with triethylammonium.[29] Similar observations were made with 6 equivalents $Et_3N$. Neither situation changed after 7 days of continuous monitoring. A sterically less hindered base butylamine was also tried, but we observed the formation of ill-defined aggregates from our $^1$H NMR experiments under the investigated parameters.

When performed in an alternate order, a sample of **2d**•Pb(II) at equilibrium was treated with $Et_3N$ and decomplexation was observed (Figure 6). The complex was disrupted and the signals from the host disappeared immediately. The final spectrum is identical to Figure 5.

We repeated these experiments with sodium carbonate and observed very small solution structure changes to the host upon addition of 2 equivalents. Unlike with triethylamine, Pb(II) complexation was NOT inhibited, nor was it accelerated (ESI, Fig. SI5). Na is unlikely to ion cap the carboxylate unlike trimethylammonium, nevertheless this did not seem to play any role in complexation rate of **2d** with Pb(II).

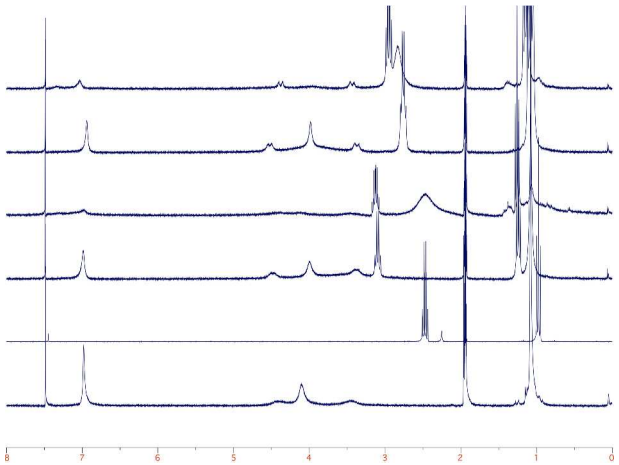

Figure 5. $^1$H NMR (300 mHz) of **2d** in presence of triethylamine in $CDCl_3/CD_3CN$ (1/1). From bottom to top: **2d**, triethylamine, **2d** + 2 eq triethylamine, **2d** + 2 eq triethylamine + 1 eq Pb(II), **2d** + 6 eq triethylamine, **2d** + 6 eq triethylamine + 1 eq Pb(II). The NMR signals are with reference to $CD_3CN$ signal at 1.94 ppm. A sharp signal at 7.49 ppm is due to $CDCl_3$.

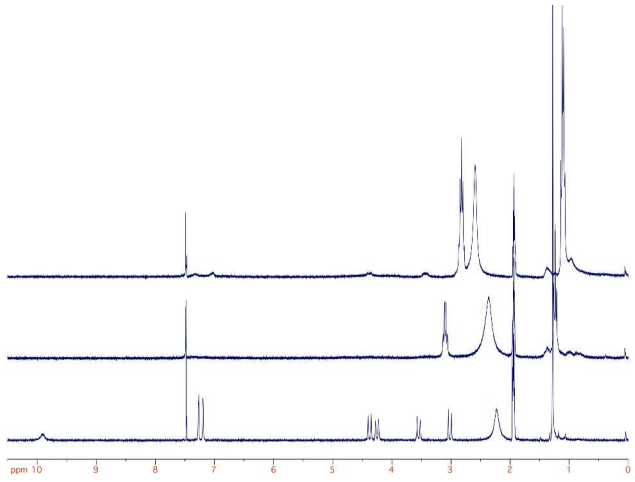

Figure 6. $^1$H NMR (300 MHz) of **2d**•Pb(II) complex upon addition of $Et_3N$ in $CDCl_3/CD_3CN$ (1/1). From bottom to top: **2d**•Pb complex, in presence of 2 eq Et3N, in presence of 6 eq $Et_3N$. The NMR signals are with reference to $CD_3CN$ signal at 1.94 ppm. A sharp signal at 7.49 ppm is due to $CDCl_3$

**Systematic exploration of the role of carboxylates**

The hexamethylester ligand **2c** also binds with Sr(II) and Ba(II) forming low symmetry 1:1 complexes (ESI Fig. SI6). These are similar to the initially formed Sr and Ba complex with **2d**, however neither evolves to a higher order complex. We reported identical results for Pb.[24] We were unable to crystallize these complexes. The carboxylic acid groups are required for

conformational switching to an octahedral complex, without which the host is unable to provide higher order coordination geometry. Mass spectral analyses are consistent with the loss of two carboxylate protons when **2d**•Ba(II) and **2d**•Pb(II) giving electroneutral complexes. The bulky t-butyl hexaester **2b** showed no major conformational change upon titration with Pb, and only minor changes for Sr or Ba (ESI Fig. SI8). Benzyl ether **2a** was also ineffective at binding (ESI Fig. SI9), thus the phenolic ether is not sufficient for binding. In one final experiment we prepared the diether host **2e**, whose methyl ether oxygen is similarly poised to the oxygens in **2c** and **2d**. Host **2e** was ineffective for binding of these cations as no changes were noted upon mixing with Sr, Pb nor Ba (ESI Fig. SI10). Thus the key functional group necessary for binding in this series of hosts is the ester, with the carboxylate being the sole means of access to extreme conformational reorganization and octahedral coordination. This final point may be due to the ability to form electoneutral complexes by loss of two hydrogens (evident from mass spectral data), or perhaps due to less inhibited movement compared to the methyl ester.

### Calix[5]arenes

The role of carboxyl groups in achieving the octahedral cage complex with **2d** with Pb(II), Sr(II) and Ba(II) is now obvious. We had already examined the binding behavior of pentamer acid **1d** with Pb(II).[30] The binding behavior of **2d** with Sr(II) and Ba(II) ions, especially the time required to emerge to a symmetrical structure made us curious to explore the binding behavior of the pentamer analog **1d** towards Sr(II) and Ba(II) ions. With **1d**, signals for both the complexed and the free ligand were observed in presence of 0.5 equivalents of Sr(II) and Ba(II), and those of free ligand vanished when the added metal was 1 equivalent of the host, the spectra remained unchanged after 15 days (ESI Fig. SI11, SI12). Thus host **1d** exhibits strong binding with high symmetry consistent with a cone conformation, but no further changes were noted upon standing. **1d** neither possesses the conformational flexibility nor the appropriate number of ligands to adopt a cage like structure around these metals. The pentaester **1b** was fixed in rigid cone conformation in $CDCl_3/CD_3CN$ (1/1) and exhibited strong affinity for binding of Pb(II), Sr(II) and Ba(II) (ESI Fig. SI13). Benzyl ether **1a** was ineffective at binding (ESI Fig. SI14). **1e** exhibited some evidence of binding with Pb(II) following conformational changes, but less so with Ba(II) and not at all with Sr(II) (ESI Fig SI15). This is somewhat distinct from the results with the calix[6]arene **2e** which did not change irrespective of metal.

## Conclusions

Sr(II), Ba(II) and Pb(II) initially form a low symmetry complex with **2d** which undergoes conformational reorganization with time to form a highly symmetrical complex, but the time required for these initially formed low symmetric complexes to come to a highly symmetrical complex is different. This is likely due to a combination of size and hardness, indeed the smaller cation Ca(II), did not bind with the hexamer acid **2d**. Based on the strong affinity of calix[5] and [6]arene esters and carboxylic acids for the binding of divalent cations and inability of alkyl derivatives lacking coordinating atom(s) other than phenoxy oxygen atom of calixarene, we hypothesized that formation of slow exchange complexes due to tighter binding of these cations with pentamer of hexamer ligands requires the proper disposition of coordinating atoms that stabilize the ligand-metal complexes due to cation-anion or cation-non bonding electron interactions. Furthermore carboxylates play a critical role when base is employed. Inorganic bases such as sodium carbonate did not play a critical role in the rate of conformational rearrangements of **2d** with Pb(II). On the other hand, organic bases such as triethyl or butylamines appeared to ion cap the ligand preventing complexation. When the preformed **2d**•Pb(II) complex was treated with organic bases, it appears to lose lead rapidly (less than 3 minutes). These subtle details of structure and reactivity are further being explored towards the use of **2d** as a potential scavenger for the environmentally malignant Pb(II) and Sr(II). These results will be reported in a sequel.

## Experimental

### General

All reagents were of reagent grade and used without further purification unless mentioned. NMR were acquired on Bruker Fourier 300-MHz or Bruker Avance III 400-MHz (NSF MRI CHE-1337559) systems. Spectra were processed (iNMR 3.5.1) using a Fourier transform with exponential weighting. NMR solvents were purchased from Cambridge Isotope Laboratories and residual solvent peak was used as an internal standard. SiliaFlash® P60 Silica Gel, 40-63 μm, 60A was purchased from Silicycle. Mass analyses were conducted at the University of California, Riverside High Resolution Mass Spectrometry Facility, Riverside, CA, USA.

### Materials

t-Butylcalix[5]arene **1** was prepared[31] and t-butylcalix[6]arene **2** was purchased from Acros Organics.

### Synthetic procedures

Compound **1a**,[32] **1b**,[22] were prepared according to the literature. **1c** was prepared by following the same protocol used for synthesis of **1b**. **1d**[30] was prepared according to the literature.

**1e** was prepared by adapting the procedure reported for a triethylene glycol analog.[33] A slurry of 0.2 g (0.246 mmoles ) **1**, 0.56 g (2.46 mmoles, 10 eq) **3** and 0.34 g (2.46 mmoles, 10 eq) $K_2CO_3$ in 8 $cm^3$ dry DMF/THF (2:1) mixture was stirred at $70^0$C for 3 days checking the progress of reaction with TLC. The reaction mixture was cooled to room temperature, THF was removed by rotary evaporation, and water was added to the remaining mixture. The resulting white precipitate was collected by filtration, washed with water, taken up in

chloroform (20 mL) and washed again with water (2x20 mL). Drying of chloroform layer (anhydrous $MgSO_4$) and solvent removal by rotary evaporation afforded an off-white solid. The crude material was then subjected to flash chromatography using 20% EtOAc in hexane to get pure product as a white solid (0.2 g, 74% yield); $R_f$ 0.21 ($SiO_2$, 20% EtOAc in Hexane). $^1H$ NMR (400 MHz, $CDCl_3$, $25^0C$) $\partial$ ppm 1.11 (s, 18H), 1.35 (s, 18H), 1.42 (s, 8H), 1.90 (bs, 2H), 2.26 (bs, 3H), 2.92 (bs, 2H), 3.18-3.91 (m, 35H), 4.18(d, J = 14 Hz, 1H), 4.37 (d, J = 13.2 Hz, 2H), 6.89 (s, 2H), 7.16 (s, 2H), 7.24 (s, 2H), 7.39 (s, 2H), 7.49 (s, 2H).

**2a**,[34] **2b, 2c,**[35] **2d**,[24] were prepared according to the literature.

Compound **2e** was obtained by adopting the procedure for the triethylene glycol analog.[33] A slurry of 0.3 g (0.3 mmoles ) **2**, 0.83 g (3.6 mmoles, 12 eq) **3** and 0.5 g (3.6 mmoles, 12 eq) $K_2CO_3$ in 10 $cm^3$ dry DMF/THF (2:1) mixture was stirred at $70^0C$ for 3 days checking the progress of reaction with TLC. The reaction mixture was cooled to room temperature and THF was removed by rotary evaporation. Addition of water to the remaining mixture resulted a thick paste, which was taken up in chloroform (20 mL) and washed with 1 M HCl (20 mL) followed by water (2x20 mL). Solvent removal from the dried organic layer by rotary evaporation afforded a crude white solid. The crude material was then subjected to flash chromatography using 20% EtOAc in hexane to get pure product as a white solid (0.16 g, 40% yield).$^1H$ NMR (400 MHz, $CDCl_3$, $25^0C$) displayed ill-defined broad signals. High temperature $^1H$ NMR improved the resolution of some signals and gave a spectrum good enough for characterizatioin. $^1H$ NMR (400 MHz, $CDCl_3$, $55^0C$) $\partial$ ppm 1.22 (s, 54H), 3.05-3.92 (bs, 54H), 7.17 (s, 12H). The compound **2e** was single spot on TLC; $R_f$ 0.44 ($SiO_2$, 20% EtOAc in Hexane) and displayed only one signal on mass spectrum at m/z 1322. $[M+H]^+$ for molecular formula $C_{84}H_{120}O_{12}$: calculated 1321.88; found 1322.

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## Notes and references

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†Electronic Supplementary Information: All preparative procedures, and new spectrosopic data are provided, NMR titrations are provided as described in the text and CIF data (CCDC 1014654) are provided. See DOI: 10.1039/b000000x/

‡ Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer using MoKα radiation (λ = 0.71073 ), operating in the ω and φ scan mode over a range of $1.00 \leq \theta \leq 24.03$, SADABS was used and the structure was solved by direct methods, all non-hydrogen atoms were refined anisotropically and disordered solvent was resolved with SQUEEZE[36] and ascribed to one $H_2O$ per unit formula, SHELXTL 97 was used for final full-matrix refinements were against $F^2$. $C_{78}H_{92}O_{19}Sr$ ($H_2O$), 1421.19 g/mol, Cubic, 28.3335(7) Å, 90.00°, 22745.8(5) $Å^3$, su max = 0.001, su mean = 0.000, 174 K, Pn-3n, Z = 8, independent reflections = 3015, R = 0.0517, wR = 0.1309 and S = 1.127.

‡ Powder X-ray diffraction data were collected, employing a PANalytical X'Pert Pro MPD diffractometer, equipped with a linear X'Celerator detector, with Cu-$K\alpha_1$ radiation. The data were collected at room temperature in the range $3^o \leq 2\theta \leq 40^o$ with ≈0.008° intervals. The X'Pert HighScore Plus software was used to determine the background, the peak positions and the peak shapes. Treor method was used to index the peaks and all the peaks were indexed based a cubic unit cell with $a$ = 28.499(4) Å.

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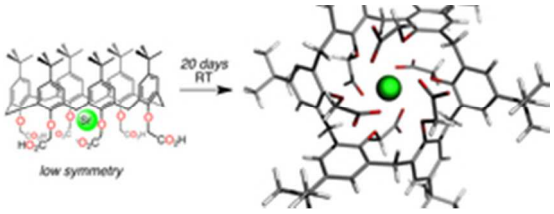


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