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Confinement of (*S*)-serine in tetra-*p*-sulfonatocalix[4]arene bilayers

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Supramolecular complexes of tetra-*p*-sulfonatocalix[4]arene and (*S*)-serine have been isolated in the solid state and their molecular structures elucidated by X-ray diffraction studies. Chiral pairs of (*S*)-serine molecules are confined in 'capsules' of tetra-*p*-sulfonatocalix[4]arene in an overall bilayer arrangement. Complexes containing differing amounts of sodium and caesium cations are reported.

Introduction

We recently described the structures of supramolecular complexes of tetra-*p*-sulfonatocalix[4]arene and racemic (alanine, histidine and phenylalanine) and chiral ((*S*)-alanine, (*S*)-histidine and (*S*)-tyrosine) amino acids (Fig. 1).[1] For alanine, histidine and phenylalanine racemic pairs of molecules are confined in capsules of the calix[4]arene in an overall bilayer arrangement. The (*S*)-amino acid isomers for alanine and histidine, however, form independent 1 : 1 complexes within the bilayer arrangement as found for many tetra-*p*-sulfonated calix[4]arene complexes. For (*S*)-tyrosine a π-stacked chiral pair of isomers is encapsulated by tetra-*p*-sulfonatocalix[4]arene.

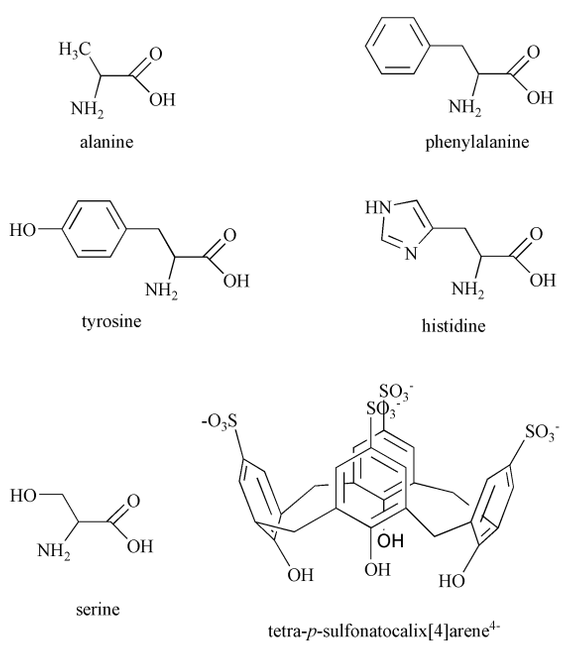

Fig. 1 Selected amino acids and tetra-*p*-sulfonatocalix[4]arene anion.

Water soluble tetra-*p*-sulfonatocalix[4]arene is a versatile host[2] and its host–guest complexes generally take on a bilayer structure with adjacent calix[4]arenes in the cone conformation alternating *via* H-bonding, π-stacking in opposite directions, and C–H ··· π interactions.[3–9] Variations of the bilayer structures are represented by 'slipped capsules' (a misalignment of the cavities of the calixarenes; which in some cases allows one sulfonyl group to be in or over the cavity of the other calixarene and *vice versa*) through to completely mismatched calixarenes in opposing layers. There are other families of calixarene supramolecular arrays, including the spheroidal and nano-tube arrangements of some calixarene complexes of lanthanides with pyridine *N*-oxide in the cavity.[4,9] There is also one example of the calixarene in the 1,3-alternate conformation, stabilised as its bipyridinium salt.[10]

Cations, be they organic,[5–7] alkali,[8,9,11,12] transition[13,14] or lanthanide metals,[3,9,15] play a crucial part in the stability and arrangement of the structures through charge balance, H-bonding, bridging and templating. The layered structures led to comparison with clay minerals and the use of the term 'organic clays'.[7–10,13,16] The structures have also been compared to lipid bilayers with respect to molecules spanning the bilayer[6] or cation channels.[1,17]

In this paper we present the isolation and structures of tetra-*p*-sulfonatocalix[4]arene encapsulated (*S*)-serine containing different ratios of sodium and caesium cations.

Results and discussion

Disodium complex

Slow evaporation of an equimolar mixture of (*S*)-serine and sodium tetra-*p*-sulfonatocalix[4]arene in acidic water (pH ~ 2.5, addition of 1 M HCl) gave colourless crystals of composition $Na_2[\{(S)\text{-serine}^+\}_2 \subset (O_3Scalix[4]arene)_2 + 4H^+] \cdot 17H_2O$ (**1**), as defined by a single crystal X-ray diffraction study. Given the ratio of calixarene to (*S*)-serine and the pH at crystallization (<2.5), some of the sulfonated groups are assumed to be protonated. The same also applies to the other two structures reported herein (see below).

Complex (**1**) crystallises in the space group *P*1 with a pair of (*S*)-serine cations encapsulated by a pair of tetra-*p*-sulfonatocalix[4]arene anions, as a 'capsule' like supermolecule. Both (*S*)-serine cations are bound to sodium cations through the C=O (Na ··· O 2.359(4) and 2.407(5) Å). One (*S*)-serine cation also binds to a sodium ion through its alcohol functionality (Na ··· O 2.537(5) Å). (*S*)-Serine cations are also involved in H-bonding to sulfonate groups through the charged NH_3^+ group (N ··· O 2.814(6), 2.839(6) Å), sodium bound water molecules (O ··· O 2.639(6) Å) and other waters of crystallisation (O ··· O 2.602(7), 2.831(6), N ··· O 2.736(8), 2.819(6) Å). The carboxylate and NH_3 groups within each (*S*)-serine cation themselves are in close proximity (N ··· O 2.631(6), 2.638(6) Å) and the OH group of the (*S*)-serine cation also participates in internal H-bonding (N ··· O 2.874(7), 2.921(7) Å). The (*S*)-serine cations are well separated within the 'capsule' except at the point where both coordinate to the same sodium cation with the OH group on one (*S*)-serine being 2.862(6) Å away from the C=O of the other.

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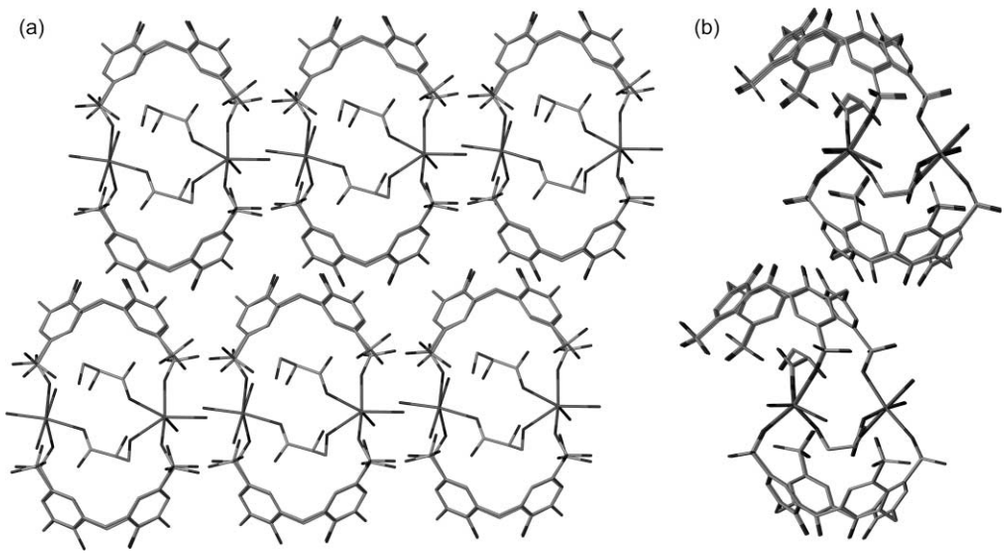

Fig. 2 Bilayer structure of (*S*)-serine encapsulated by tetra-*p*-sulfonatocalix[4]arene in the disodium complex (**1**).

Sodium cations are bound to two sulfonate groups (one from each calix[4]arene anion in the 'capsule'; Na ··· O 2.442(4), 2.439(5), 2.486(4), 2.432(6) Å). Three terminal water molecules complete one Na^+ coordination sphere (Na ··· O, 2.319(5), 2.438(4), 2.469(4) Å), and two terminal water molecules complete the other coordination sphere (Na ··· O, 2.385(6), 2.506(6) Å), which leads to independent sodium bridged 'capsules' (Fig. 2).

The polar groups of (*S*)-serine cations point away from the hydrophobic calix[4]arene bowl as would be expected, leaving (*S*)-serine cations sitting in the rim of the sulfonatocalix[4]-arene anions. Overall the structure has the bilayer arrangement of up/down alternating calix[4]arenes separated by a hydrophilic layer containing the (*S*)-serine and sodium cations and water molecules.[2,3]

The calix[4]arene cone conformation optimises the usual phenol group H-bonding (O ··· O distances, 2.63–2.67 Å). The tetra-*p*-sulfonatocalix[4]arene 'capsule' is held together by coordinated sodium ions (S ··· S separations 7.3(1) and 6.9(1) Å and shortest O ··· O separation 4.721(6) Å between the two calixarenes).

Pentasodium complex

Slow evaporation of an equimolar mixture of (*S*)-serine and sodium tetra-*p*-sulfonatocalix[4]arene in acidic water (pH ~ 2.5, addition of 1 M HCl) in the presence of NaCl (four-fold excess) gave colourless crystals of composition $Na_5[((S)\text{-serine}^+)_2 \subset (SO_3\text{calix[4]arene})_2 + H^+]\cdot 15H_2O$ (**2**). The complex also crystallises in the chiral space group *P*1 with a pair of (*S*)-serine cations encapsulated by a pair of tetra-*p*-sulfonatocalix[4]-arenes.

Both (*S*)-serine cations are bound to sodium cations through the C=O (Na ··· O 2.583(5) and 2.508(12) Å) as in (**1**). (*S*)-Serine cations are also involved in H-bonding to sulfonate groups through the charged NH_3^+ group (N ··· O 2.754(10), 2.888(8) Å) and through the OH in one case (O ··· O 2.793(6) Å). Other H-bonds are to sodium bound water molecules (N ··· O 2.716(12); O ··· O 2.484(23), 2.910(11), 2.637(10), 2.588(7), 2.903(11), 2.868(7) Å) and other waters of crystallisation (N ··· O 2.817(7), 2.825(7), 2.831(8); O ··· O 2.701(7), 2.887(6) Å). The carboxylate and NH_3 groups within each (*S*)-serine cation themselves are in close proximity (N ··· O 2.654(6), 2.484(11) Å) and the (*S*)-serine cation alcohol OH also participates in internal H-bonding (N ··· O 2.851(9), 2.889(8) Å). The pair of (*S*)-serine cations are well separated within the 'capsule' with the alcoholic oxygen on one (*S*)-serine being 3.194(7) Å away from the C=O of the other. The two (*S*)-serine cations H-bond through common waters of crystallisation.

Each sodium cation is connected to another sodium atom either through coordination to a common water molecule or oxygen on a sulfonate group. Three sodium cations are six co-ordinate, binding to two separate sulfonate groups (Na ··· O 2.341–2.538 Å and in the Na ··· O ··· Na cases Na ··· O 2.550–2.675 Å) and have bridging (Na ··· O 2.369(6), 2.461(6) Å) and/or terminal water molecules (Na ··· O 2.267–2.654 Å) and/or (*S*)-serine cations (Na ··· O 2.508(12), 2.583(5) Å) completing their coodination sphere. Two sodium cations are five coordinate, binding to three separate sulfonate groups (Na ··· O 2.304–2.438 and in the Na ··· O ··· Na case; Na ··· O 2.408(5) Å) and have bridging (Na ··· O 2.362(6), 2.403(5) Å) and/or terminal water molecules (Na ··· O 2.306–2.335 Å) completing their coodination sphere (Fig. 3). As a consequence, each bis-calix[4]arene 'capsule' is held together by two sodium cations, and bridge *via* sodium cations to all six nearest neighbour 'capsules' within the hydrophilic layer structure. Four additional 'capsules' interact both above and below in the hydrophobic layer with coplanarity of the aromatic rings separated by more than 3.6 Å and with limited overlap of bonds. This contrasts to the many examples where there exist closer contact with good overlap of the π-systems as well as the phenol–sulfonate H-bonding.[9]

The polar groups of (*S*)-serine cations again point away from the hydrophobic calix[4]arene bowl leaving (*S*)-serine cations sitting in the rim of the tetra-*p*-sulfonatocalix[4]arene anions. As for (**1**), the structure has the bilayer arrangement of up–down alternating calix[4]arenes separated by a hydrophilic layer containing the (*S*)-serine and sodium cations and water.[2,3] However, encapsulation is now best described by a 'slipped capsule' due to off-centre alignment of the calix[4]arene layers (Fig. 3). The 'slipped capsule' is held together by coordinated sodium ions (S ··· S separations 6.708–7.485 Å and shortest O ··· O separation, 4.181(7) Å between the two calixarenes). As in (**1**) the cone conformation of the calix[4]arene optimises phenolic OH H-bonding (O ··· O distances, 2.625–2.695 Å).

Overall the structure retains the bilayer arangement normally seen for tetra-*p*-sulfonatocalix[4]arenes, with a complex array of sodium cations sitting between the hydrophobic surfaces of the bilayers, binding adjacent calixarenes into a coordination network. The associated channeling of sodium ions is of interest as evident in Gokel's recent discussion on the formation of networks of sodium ions in channel-like arrays in the presence of a variety of donor groups with particular respect to mimicing natural cation channels within phospholipid bilayers.[16]

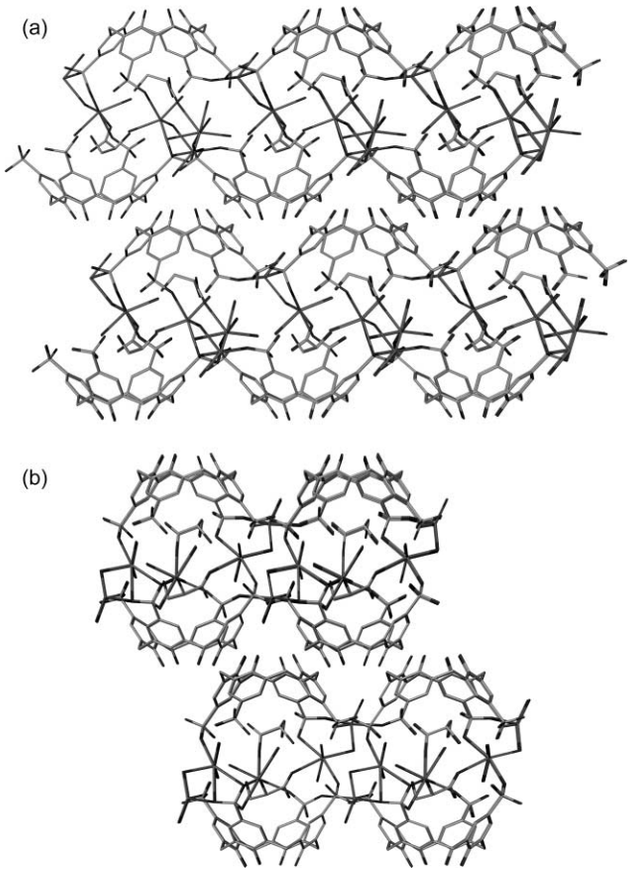

Fig. 3 Bilayer structure of (*S*)-serine encapsulated by tetra-*p*-sulfonatocalix[4]arene in the pentasodium complex (**2**).

Dicaesium–disodium complex

Slow evaporation of an equimolar mixture of (*S*)-serine and sodium tetra-*p*-sulfonatocalix[4]arene in acidic water (pH ~ 2.5, addition of 1 M HCl) in the presence of CsBr (two fold excess) gave colourless crystals of composition $Cs_2Na_2(Cl)$-[{(*S*)-serine$^+$}$_2$⊂(O_3Scalix[4]arene)$_2$ + $3H^+$]·$11H_2O$, (**3**). An X-ray diffraction study showed that the complex also crystallises in space group *P*1, with a pair of (*S*)-serine cations encapsulated by a two tetra-*p*-sulfonatocalix[4]arenes, and with the incorporation of a chloride anion for the first time in the series of amino acid tetra-*p*-sulfonatocalix[4]arenes complexes crystallised from dilute HCl solutions.

As for (**1**) and (**2**), the structure of (**3**), has both (*S*)-serine cations bound to the same sodium cation through the C=O (Na ··· O 2.426(6) and 2.467(6) Å), but now with one (*S*)-serine cation binding through the same oxygen to a caesium cation (Cs ··· O 3.202(5) Å). (*S*)-Serine cations are also involved in H-bonding to sulfonate groups through the charged NH_3^+ group (N ··· O 2.878(7), 2.918(9), 2.968(8) Å). Other H-bonds are to sodium bound water molecules (N ··· O 2.837(7); carboxy hydroxy O ··· O 2.673(8), 2.697(8) Å) and other waters of crystallisation (alcohol hydroxy O ··· O 2.695(7), 2.667(8) Å). The carboxylate and NH_3 groups within each (*S*)-serine cation themselves are in close proximity (N ··· O 2.632(8), 2.667(8) Å) and the (*S*)-serine cation OH group also participates in internal H-bonding (N ··· O 2.854(8), 2.870(8) Å). The pair of (*S*)-serine cations are situated within the 'capsule' such that the alcoholic oxygen on one (*S*)-serine cation H-bonds to NH of the other (*S*)-serine cation (N ··· O 2.985(9), 3.010(9) Å).

Both sodium cations are six coordinate, with one sodium cation binding to both (*S*)-serine cations through the carboxy oxygen (Na ··· O 2.467(6), 2.426(6) Å), two sulfonate group oxygens (Na ··· O 2.302(7), 2.431(6) Å) with bridges to a caesium cation water molecule (Na ··· O 2.391(6) Å) and a terminal water molecule (Na ··· O 2.377(7) Å) completing the coordination sphere. The second sodium cation binds to four sulfonate group oxygens (Na ··· O 2.290(6), 2.381(6), 2.423(5), 2.474(5) Å) with two terminal water molecules completing its coordination sphere (Na ··· O 2.355(6), 2.449(5) Å). Both sodium cations bridge the calix[4]arene anions in the 'capsule' with the second sodium cation also acting to bridge two calix[4]arene anions in an adjacent 'capsule' leading to a chain of sodium bridged 'capsules'.

Both caesium cations bridge calix[4]arene anions within a 'capsule' and both bridge adjacent 'capsules' which results in the caesium cations being between and linking the sodium bridged chains of calix[4]arene 'capsules' (Fig. 4). One caesium cation is nominally eight coordinate with five bonds to sulfonate groups originating from two adjacent 'capsules' (Cs ··· O 2.950(6), 3.020(5), 3.119(5), 3.147(9), 3.148(9) Å), a bond to the (*S*)-serine carboxy oxygen (Cs ··· O 3.202(5) Å) and two long bonds to bridging water molecules (Cs ··· O 3.343(6), 3.457(9) Å). The second caesium cation is six coordinate, with four bonds to sulfonate group oxygens from three adjacent 'capsules' (Cs ··· O 3.009(6), 3.104(6), 3.149(5), 3.242(4) Å), one bond to a bridging water molecule (Cs ··· O 2.945(8) Å) and a bond to the chloride anion (Cs ··· Cl 2.905(3) Å).

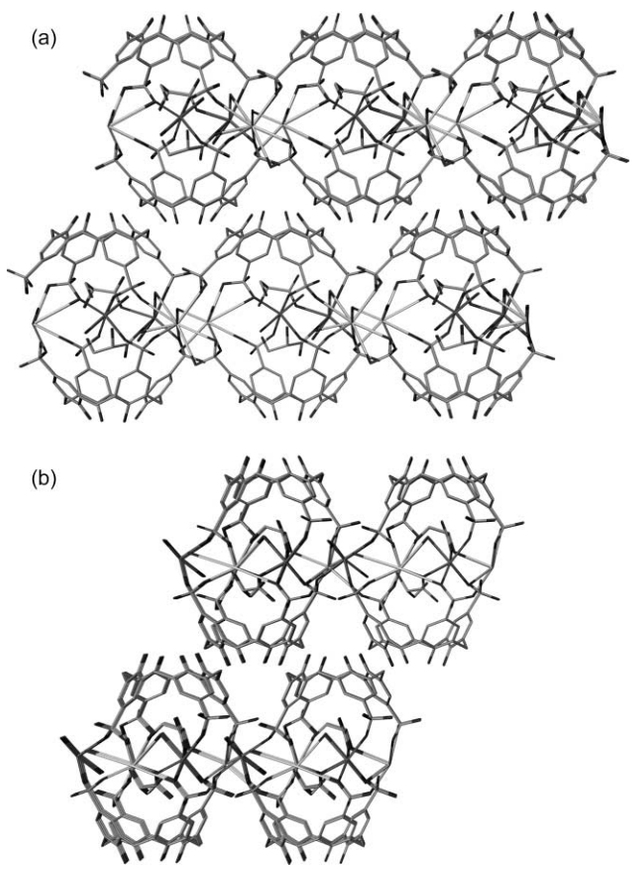

Fig. 4 Bilayer structure of (*S*)-serine encapsulated by tetra-*p*-sulfonatocalix[4]arene in the disodium–dicaesium complex (**3**).

The polar groups of (*S*)-serine cations again point away from the hydrophobic calix[4]arene bowl leaving (*S*)-serine cations sitting in the rim of the tetra-*p*-sulfonatocalix[4]arene anions. Overall the structure has the bilayer arrangement of up–down alternating calix[4]arenes separated by a hydrophilic layer containing the (*S*)-serine, caesium and sodium cations and water[2,3] (Fig. 4).

The calix[4]arene cone conformation is stabilised by the usual phenol group H-bonding (O ··· O distances, 2.662–2.727 Å). The tetra-*p*-sulfonatocalix[4]arene capsule is held together by coordinated sodium ions (S ··· S separations 4.697–5.992 Å

Table 1 Crystallographic details

Compound	**1**	**2**	**3**
Formula	$C_{62}H_{88}N_2O_{55}S_8Na_2$	$C_{62}H_{87}N_2O_{53}S_8Na_5$	$C_{62}H_{81}N_2O_{49}S_8Cl_1Cs_2Na_2$
M_w/g mol^{-1}	2043.80	2079.77	2242.02
Size/mm	0.15 × 0.15 × 0.12	0.15 × 0.15 × 0.10	0.18 × 0.15 × 0.14
System	Triclinic	Triclinic	Triclinic
Space group	*P*1 (no. 1)	*P*1 (no. 1)	*P*1 (no. 1)
a/Å	11.8958(1)	11.7834(1)	11.6093(1)
b/Å	12.0330(1)	12.3597(2)	12.3864(1)
c/Å	15.7894(2)	15.4799(2)	15.6609(2)
α/°	99.4184(4)	83.0758(7)	69.5758(4)
β/°	108.4511(5)	67.8400(8)	73.7510(4)
γ/°	90.1235(5)	89.7123(5)	89.8427(5)
V/Å^3	2111.53(4)	2070.72(5)	2014.82(4)
Z, D_c/g cm^{-3}	1, 1.607	1, 1.668	1, 1.848
μ/cm^{-1}	3.35	3.56	12.72
$2\theta_{max}$/°	56.66	56.58	56.64
R	0.0684	0.0659	0.0584
R_w	0.174	0.157	0.160
Refns. (total)	38710	35201	36215
Refns. (unique)	19318	18956	18658
Refns. (obsd)	15874	13634	16560
CCDC no.	202923	202924	202925

and shortest O ··· O separation, 3.158(6) Å between the two calixarenes).

Conclusion

All the structures of tetra(*p*-sulfonated)calix[4]arene hosting amino acids show that the amino acids are well accommodated by the calixarene with strong hydrogen bonding. The bilayer structures are closely spaced with the repeat distances being within 14–15 Å, just a little longer than the distance in the hydrated sodium salt (Na_4[tetra(*p*-sulfonatocalix[4]arene·$12H_2O$), 13.7 Å[8] but significantly shorter than for the adeninium salt, 19.1 Å.[7] The inorganic layers are between 7.7 and 8.9 Å thick compared to the 8.3 Å value for the sodium salt and 14.7 Å for the adeninium complex.

Within the amino acid tetra(*p*-sulfonated)calix[4]arene complexes studied we have found alkali metal to proton content ranging from 1 : 5 (for (*R*,*S*)-alanine) through 2 : 4 ((*R*,*S*)-histidine, (*S*)-histidine, (*R*,*S*)-phenylalanine and (*S*)-serine), 7 : 7 (for the 1 : 2 (*S*)-tyrosine–calixarene complex), 4 : 3 (Na–Cs (*S*)-serine complex), 5 : 1 ((*S*)-serine) to the 6 : 0 value for the proton free (*S*)-alanine complex. All the structures consist of bilayers with the alkali metals lying in the hydrophilic layer and binding across sulfonato groups of the tetra(*p*-sulfonated)-calix[4]arene. The apparent readiness to accommodate a varying number of protons and alkali metals support the 'clay-like' description.[7–10,13,16]

The only other amino acid tetra(*p*-sulfonated)calix[4]arene structure reported involves (*S*)-lysine with no alkali metal cations present and charge balance being through the 2 : 1 ratio of the the (*S*)-lysine dications to the tetra(*p*-sulfonated)-calix[4]arene anion.[6] In this case the (*S*)-lysine dications span the bilayer.

Experimental

All reagents were commercial products of high purity and were not further purified except tetrasodium tetra-*p*-sulfonatocalix-[4]arene which was prepared *via* the reaction of sulfuric acid with tetra(*tert*-butyl)calix[4]arene.[18] Crystals of the complexes discussed were grown by evaporation of aqueous acid (pH ~ 2.5, addition of 1 M HCl) solutions of tetrasodium tetra-*p*-sulfonatocalix[4]arene, (*S*)-serine and any added salt as indicated. The complexes tended to lose water of crystallisation rapidly and the presence of precipitated starting materials made bulk microanalyses unreliable.

Crystallography

All crystals were mounted onto a glass capillary under paraffin oil. X-Ray data were collected at 123(1) K on an Enraf-Nonius KappaCCD single crystal diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods with SHELX-97[19] and refined by full matrix least-squares on F^2 ($I > 4\sigma(I)$) using the X-Seed[19] interface for SHELX-97. Data was corrected for Lorentzian and polarisation effects, but not absorption. The non-hydrogen atoms were refined anisotropically (with the exception of C8 and C40 in complex (**3**) which were refined isotropically: other similar carbon atoms in complex (**3**) had low thermal parameters). None of the hydrogen atoms were refined but hydrogen atoms attached to carbon atoms were included at geometrically estimated positions. Crystallographic data are summarised in Table 1.

CCDC reference numbers 202923–202925.

See http://www.rsc.org/suppdata/dt/b3/b301316b/ for crystallographic data in CIF or other electronic format.

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