

Self-Assembled Superanions: Ionic Capsules Stabilized by Polynuclear Chromium(III) Aqua Cations

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Abstract: Aqueous solutions of sodium *p*-sulfonatocalix[4]arene and 18-crown-6 containing purified, polynuclear hydrolytic Cr^{III} cations [Cr₂(OH)₂(H₂O)₈]⁴⁺, [Cr₃(OH)₄(H₂O)₁₀]⁵⁺ or [Cr₄(OH)₆(H₂O)₁₂]⁶⁺ (as their perchlorates) at about pH 2 afford crystalline, extensively hydrated complexes. These complexes contain the Cr^{III} complex cations and self-assembled globularlike superanions or ionic capsules [Na⁺ ⊂ (18-crown-6)-

(OH₂)₂] ⊂ {(*p*-sulfonatocalix[4]arene⁴⁻)₂}]⁷⁻, which are triply, doubly or singly protonated, respectively. The superanions possess a central sodium ion bound by a crown ether and two *trans*

water molecules; this moiety is further shrouded by two calixarenes. The di- and trinuclear cations can be leached from the solid complexes by treatment with aqueous HClO₄, and the complex containing the tetranuclear species is selectively formed from a solution containing a mixture of the various polynuclear cations.

Keywords: calixarenes · chromium · ionic capsules · polynuclear cations · self-assembly · supramolecular chemistry

Introduction

Large, highly charged ions are important for the formation of micelle-like species and other nano-sized structures in solution, for the development of enzyme models and for crystal engineering in preparation of complex assemblies in the solid state.^[1–10] Bowl-shaped and highly charged, water soluble sodium *p*-sulfonatocalix[4,5]arenes can form claylike bilayer structures that show remarkable inclusion properties, encompassing ionic guests and molecules,^[3–5] including water, in the hydrophobic cavity associated with H₂O ⋯ π-aromatic hydrogen bonding.^[6] We now report that from solutions of sodium *p*-sulfonatocalix[4]arene in the presence of 18-crown-6 at around pH 2, the self-assembly of globular-like superanions or ionic capsules with axial symmetry occurs. These capsules contain a central sodium ion bound by a crown ether and two *trans* water molecules; this moiety is further shrouded by two calixarenes. The superanions are effectively inclusion complexes of inclusion complexes, and the cohesion in the solid state comes from interplay of different supramolecular interactions, notably hydrogen-bonding, electrostatic, π-stacking and van der Waals interactions. Self-assembly of analogous molecular capsules has been achieved through hydrogen bonding,^[11–19] and both cationic^[20] and anionic^[21] capsules have been generated through metal–ligand coordination.

The superanions are versatile charge reservoirs with a common structural motif; they can facilitate the crystallization of polynuclear transition metal aqua ions with different charge, size and shape. Indeed this has led to the structural authentication of the nonlabile polynuclear hydrolytic Cr^{III} cations [Cr₃(OH)₄(H₂O)₁₀]⁵⁺ and [Cr₄(OH)₆(H₂O)₁₂]⁶⁺ for the first time.^[22] The only previously characterised species in the series is the lowest oligomer, the dinuclear cation [Cr₂(OH)₂(H₂O)₈]⁴⁺; the analogous nonlabile, dinuclear Rh^{III}^[23] and mixed Cr^{III} and Rh^{III} species are the only authenticated cations in their respective homologous series.^[24] Furthermore, the superanion has been found to selectively bind the cations according to size and shape. These findings open the possibilities of confinement of other cations in the core of the superanion assembly, the binding and stabilization of large, highly charged cations in general and the formation of ionic capsules based on more than two calixarenes that shroud large cations.

Results and Discussion

Treatment of an oligomeric mixture of polynuclear Cr^{III} aqua ions^[25] with aqueous solutions of Na₄{*p*-sulfonatocalix[4]arene} and 18-crown-6 at around pH 2 results in the selective binding of the tetranuclear [Cr₄(OH)₆(H₂O)₁₂]⁶⁺ with the superanion [X+H⁺]⁶⁻, X = {Na⁺ ⊂ (18-crown-6)(OH₂)₂] ⊂ {(*p*-sulfonatocalix[4]arene⁴⁻)₂}]⁷⁻, to give compound **1**. Compound **1** crystallizes as pale green crystals with a large component of water molecules, Figure 1. The hydrolytic Cr^{III} dinuclear and

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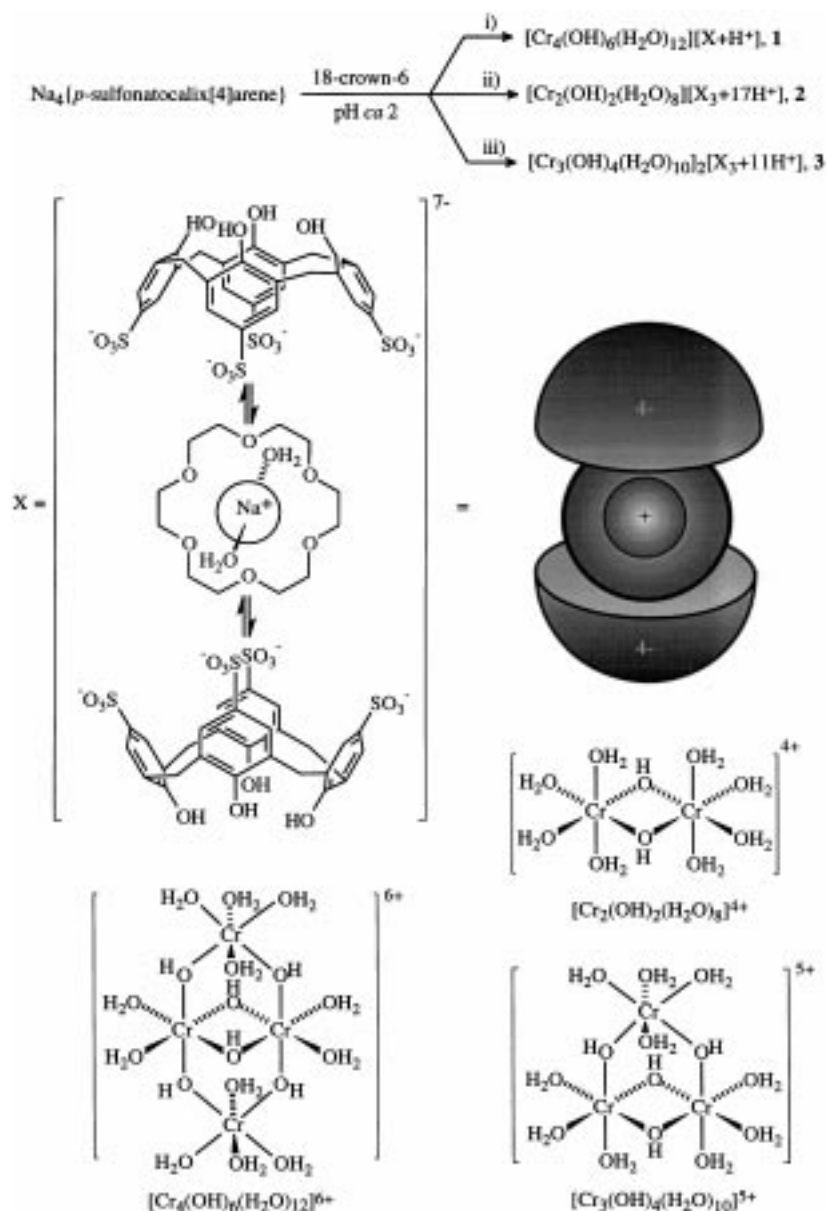


Figure 1. Synthesis of the hydrates of **1**, **2** and **3**. Conditions for the generation of the chromium cations used in i)–iii): a mixture of Cr^{III} aqua ions formed on treating a solution containing $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ with aqueous base followed by immediate quenching with HClO_4 generates a series of polynuclear Cr^{3+} aqua ions (% Cr), dinuclear $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ (8%), trinuclear $[\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}]^{5+}$ (13%), tetranuclear $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$ (10%), higher oligonuclear species (64%) and unreacted $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (5%).^[25] i) $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}][\text{ClO}_4]_6$; ii) purified solution of $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8][\text{ClO}_4]_4$; iii) purified solution of $[\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}][\text{ClO}_4]_5$.

trinuclear cations also form crystalline complexes with the same superanion (**2** and **3**), albeit from pure solutions of the respective oligomers. The overall yields of the dimer and trimer complexes are $\sim 60\%$ based on calixarene, which is the limiting reagent. Maintaining the solution at less than pH 3 is required in order to stabilize the polynuclear cations towards the formation of higher polynuclear species.^[22, 25] In the solid state the ratio of cation to anion is 1:1 for the system with the tetranuclear cation, 2:3 for the trinuclear cation and 1:3 for the dinuclear system; these data were established by X-ray diffraction data and electron-microprobe analysis.

The ratio of cations to anions in the solid state is maintained for each system even when varying the ratios of calixarene:

crown ether and calixarene: polynuclear cations, despite the different charge and size of the cations. This highlights a remarkable property of the superanion, that is, the ability to accommodate different charged species by varying the degree of protonation of the sulfonate groups. In the case of the dinuclear and trinuclear cations this is achieved within the same packing array of the superanions. Addition of excess crown ether over calixarene still gives the same complexes. This is an important consideration in the X-ray structure determinations, since any residual electron density within the lattice must be associated with water molecules rather than sodium ions, which would be bound by a crown ether.

The solid-state structure of the Cr^{III} tetranuclear species $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}[\text{X}+\text{H}+]^{6-}$ (**1**), with 31 molecules of water of crystallization, was established from X-ray diffraction data at 123 K. The structure of the superanion assembly, Figure 2a, shows Na^+ as the central core bound to the 18-crown-6 and two *trans*-water molecules to form the $\{\text{Na}^+ \subset (\text{18-crown-6})-(\text{OH}_2)_2\}$ moiety. This moiety fits snugly into two calixarenes, held together by hydrogen bonds between the two water molecules and sulfonate groups, and the hydrophobic complementarity of the peripheral of the crown ether with the cavity of the calixarenes. Complementarity of curvature of the crown

ether with that of the calixarene is achieved by two opposite phenol groups being splayed apart, dihedral angle 91° , relative to the other two, dihedral angle 46° . Presumably the collective energies of hydrogen bonding of the sodium-bound water molecules ($\text{S}-\text{O} \cdots \text{H}_2\text{O}-\text{Na}$), electrostatic interactions and van der Waals interactions within the cavities of the calixarenes is greater than the energy associated with inclusion of water molecules in the cavities through $\text{H}_2\text{O} \cdots \pi$ -aromatic-hydrogen interactions.^[6]

The anions reside on inversion centres, but their overall symmetry (ignoring any protons on the sulfonate groups) approximates to D_{2h} . They are essentially globular with axially dependant surface properties, alternating hydrophilic

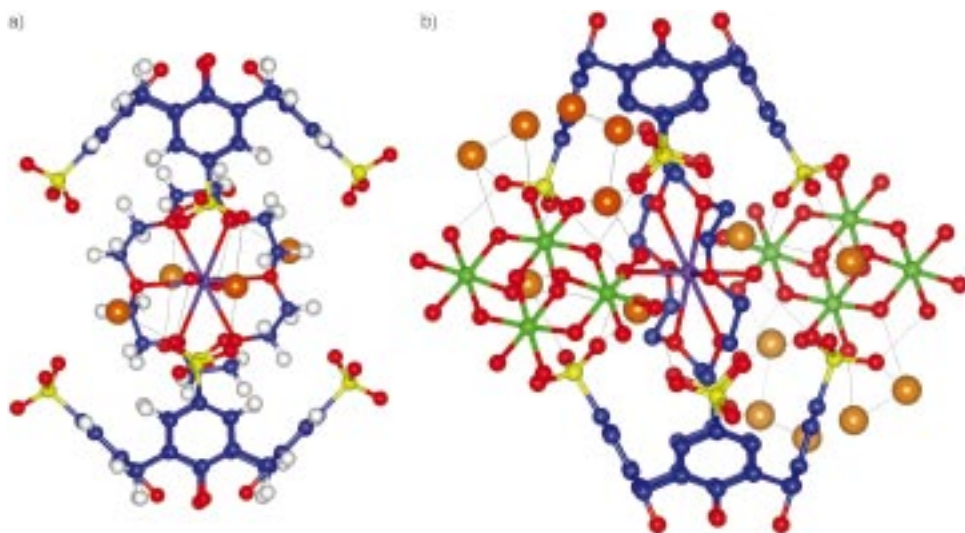


Figure 2. Projections of the structure of hydrated compound **1**, showing a) the superanion assembly with hydrogen-bonded water molecules in orange and b) the interplay of all components. The fine black lines indicate hydrogen-bonding interactions.

and hydrophobic in the direction of the principle axis: hydrophilic for the OH group, hydrophobic for the aromatic rings, hydrophilic for the two adjacent sets of sulphonate groups (and associated water molecules), then hydrophobic and hydrophilic. This Jovian array relates to how the anions pack in the solid state; this appears to be driven by π stacking between aromatic rings of adjacent superanions, with each calixarene forming π – π interactions with three other calixarenes within the crystal lattice at ring centroid separations of 3.77, 3.81 and 4.28 Å.

The structurally characterised Cr^{III} tetranuclear cation in **1** sits at the periphery of the hydrophilic sulphonate equator of the superanion, with each cation forming hydrogen-bonding interactions with two superanions (Figure 2b). Tetranuclear $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$ is cyclic and lies across a crystallographic inversion centre with two types of Cr centres. One is coordinated by two terminal water molecules and four μ -OH-bridging ligands, with a double bridge to an equivalent Cr centre, at a Cr...Cr separation of 2.929(1) Å, and a single bridge to the other type of Cr centre, at a Cr...Cr separation of 3.585(1) and 3.599(1) Å. This second Cr centre is coordinated by four terminal waters and two μ -OH-bridging ligands. Cr–O distances range from 1.944(3) to 2.003(3) Å, which is consistent with those found for $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$.^[26] The cyclic nature of the observed structure is similar to that proposed on the basis of solution studies; however, there is no evidence of the proposed μ_3 -OH^[22] here. The cation to anion ratio is 1:1, hence the overall charge of the superanion is 6–, which equates to protonation of one sulphonate group of the superanion. Numerous water molecules sit within the crystal lattice at hydrogen-bonding distances to both the anion and cation.

The structures of the hydrates of the dinuclear and trinuclear species $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8][\text{X}_3+17\text{H}^+]$ (**2**) and $[\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}][\text{X}_3+11\text{H}^+]$ (**3**) were also established from X-ray diffraction data at 123 K. The supramolecular structures are similar despite the differences in cation ratios and identities, as is evident from the similarity in unit-cell

parameters, and the degree of protonation of the superanions, which should be regarded as tentative (see later) unlike in **1**. The atom-to-atom connectivity of the dinuclear cation is unexceptional^[26] and that of the trinuclear cation is similar to that proposed on the basis of solution studies.^[22] The structures and crystal packing of the superanions are essentially the same in both structures. There are two types of superanion, one of which lies across an inversion centre, that are structurally distinguished by slightly different degrees of pitch of aromatic rings in the calixarenes. The dihedral angles between opposite phenol groups

are 59° and 83° for one superanion and 48° and 100° for the other. It is notable that the closest S–O...O–S distances of opposed calixarenes in the superanions are closer for **2** and **3** than for **1** (ca. 5.8 cf. 6.3 Å). Packing of the superanions within the crystal lattice is different to that seen for **1** and incorporates both π stacking with ring–centroid distances of 3.82, 3.89 and 4.04 Å and, unlike in **1**, O–H...O–S hydrogen bonds between calixarenes of adjacent superanions (Figure 3).

The cation to anion ratios for **2** and **3** were established by electron-microprobe analysis and analysis of displacement parameters within the crystal structures. Both techniques

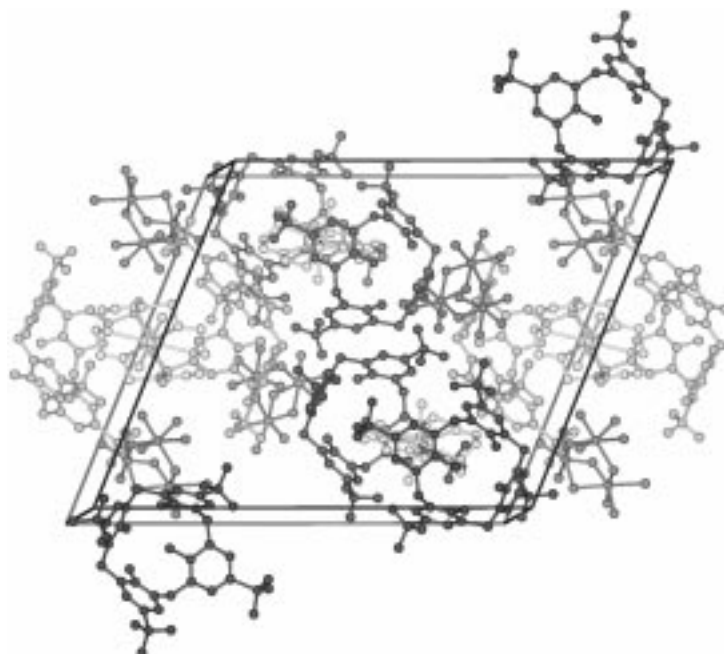


Figure 3. Packing diagram of **3** viewed along the *a* axis. The cation is disordered over three sites, two of which are superimposed—one of the superimposed cation positions and disordered water molecules have been omitted for the sake of clarity. The structure of **2** has the same superanion packing and has disordered cations.

indicated similar results with a 1:2 dinuclear cation to superanion ratio (1:3 Cr to Na ratio) in **2**, and a 2:3 trimer cation to superanion ratio (2:1 Cr to Na ratio) in **3**. In both cases the cations are disordered. For **2** the dinuclear cation is present at one site of the asymmetric unit with a partial occupancy of 0.25. On the other hand, the trinuclear cation in **3** is disordered over three sites, each with an occupancy of 0.33. Two of these sites show partial overlap of the trinuclear units. The extreme disorder of the dinuclear and trinuclear cations means that the determination of their geometric parameters with a high degree of reliability is not possible; however, their gross structural features can be established. The structure of the dinuclear cation is in agreement with that reported by Spiccia et al.,^[26] while the hitherto structurally unauthenticated trinuclear cation has a cyclic μ -OH-bridged structure (Figure 3) similar to that found for the tetranuclear complex, with the three Cr positions forming a triangle at approximate Cr...Cr distances 2.86(1), 3.50(1) and 3.56(1) Å. The trimer is isostructural with a cyclic form of the analogous Rh^{III} trimer proposed from solution studies.^[27]

The structures of **2** and **3** have a large number of disordered water molecules, some of which hydrogen bond to the cations and anions. Charge balance can be rationalised by protonation of sulfonate groups. As was seen for **1** the superanions are part of the secondary coordination sphere of the transition metals clusters through extensive hydrogen bonding. The disordered dinuclear cations in **2** are associated with only one of the two types of superanions, while in **3** both types of superanions form weak interactions with the disordered cations. It should be stressed, however, that the actual number of anion-to-cation interactions are less than this owing to the partial occupancy of the cations. The collective energetics of these interactions together with the intra-superanion hydrogen-bonding and π stacking are, presumably, important in the overall cohesion of the structure, especially given that electrostatic attraction of the internal sodium cation is unlikely to compensate for the electrostatic repulsion between the deprotonated calixarenes.

The transition metal cations may initially act as a clamp for the two calixarenes of each supermolecule. In the case of **1**, the tetranuclear species forms hydrogen bonds to the sulphonates of all four calixarenes of adjacent superanions to create a large supramolecular entity. This extra mode of stabilization is not as readily available to the dinuclear- and trinuclear-containing systems owing to geometric considerations; the cations are not large enough to span four calixarenes and are only partially incorporated within the crystal lattices. Additional stability may be provided by closer inter-superanion interactions than those seen in **1** and additional water-superanion interactions.

The Cr^{III} oligomers can be irreversibly leached out of crystalline hydrated **2** and **3** by treatment with aqueous HClO₄, leaving a white crystalline powder, whereas similar treatment of **1** results in its dissolution and solvation of the tetranuclear species.^[19] Mononuclear [Cr(H₂O)₆]³⁺ does not form a superanion complex under the same conditions, which includes a pH close to 2; the lower charge on the mononuclear cation (3+, cf. 4+, 5+ and 6+ for **2**, **3** and **1**, respectively) must be insufficient to compensate for the electrostatic

repulsion between the calixarenes within the superanions. Given that the ratio of cations to superanions in **2** and **3** is <1, the cations may be in part leached from the solid once the superanions are formed with charge compensation by protons from the strongly acidic medium. There are channels laden with water molecules (and cations) in the two structures that are large enough for such a process. The higher charge and size of the cations in **1** results in the cations being trapped in the lattice.

Conclusions

Generation of the superanions relies on the formation of a large number of supramolecular interactions that interplay in concert. The ability to have control over all of these within the same system, and for different highly charged cations, is remarkable, and the ground rules established have relevance for the building of systems with different core cations and different multiply charged cations, leading to larger superanions. The crystallization of polynuclear aqua ions has been a challenging problem. One of the more successful methods is a supramolecular approach that uses aromatic sulfonates as counter ions. This method relies on the formation of layers of aqua cations and water molecules stabilized in a hydrogen-bonded network by suitably oriented layers of sulfonate anions and, more recently, by the inclusion of crown ether molecules in this network.^[26, 28] However, this technique has only allowed the structural X-ray authentication of some oxo- and hydroxo-bridged binuclear aqua ions, such as [Cr₂(μ -OH)₂(H₂O)₈]⁴⁺,^[26, 28] [Rh₂(μ -OH)₂(H₂O)₈]⁴⁺,^[23] [CrRh(μ -OH)₂(H₂O)₈]⁴⁺,^[24] and a Mo^{IV} trinuclear species.^[29] Although studies of the hydrolytic polymerisation of Cr³⁺ and Rh³⁺ has led to the isolation and solution characterisation of several oligomers,^[22, 23] attempts to crystallize oligomers with a higher nuclearity than dinuclear species have been unsuccessful. The superanion or ionic capsule approach demonstrates a new general method for the structural characterisation of metal ions present in aqueous systems. This has implications for a better understanding of the hydrolytic polymerisation reactions of metal ions in solution; these are of fundamental importance and occur widely in biological systems, industrial processes and natural waters. There is also scope for stabilizing large organic and biological cations.

Experimental Section

Synthesis: Details of the synthesis of the hydrates of **1–3** are given in Figure 1. Crystalline material suitable for single crystal X-ray diffraction studies deposited over several days in ca 60% yield. Electron-microprobe analyses gave ratios of cations to anions consistent with the structure determinations.

Crystal structure determinations: All X-ray structural data were collected on an Enraf-Nonius KappaCCD diffractometer with MoK α radiation ($\lambda = 0.71073$ Å) at $T = 123$ K. Data were corrected for Lorentzian polarisation but not absorption. The structures were solved by direct methods with SHELXS-97^[30] and refined by full matrix least-squares on $|F^2|$ with SHELXL-97.^[31]

Crystal structure of [1·31(H₂O)]_{0.5}: C₃₄H₆₅Cr₂Na_{0.5}O_{44.5}S₄, $M = 1429.6$ g mol⁻¹; triclinic, $P\bar{1}$, $a = 13.4803(4)$, $b = 14.2163(4)$, $c = 17.7347(7)$ Å, $\alpha = 104.477(1)$, $\beta = 109.611(1)$, $\gamma = 97.779(1)^\circ$, $V = 2946.4(2)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.61$ g cm⁻³, $F(000) = 1493$, $\mu_{\text{Mo}} = 0.628$ mm⁻¹ (no correction), size $0.30 \times$

0.23 × 0.23 mm, $2\theta_{\max} = 56.6^\circ$, 790 parameters, final $R_1 = 0.073$ (observed data), $wR_2 = 0.2282$ [all data, weights $w = 1/[\sigma^2 F_o^2 + 0.1195 P^2 + 8.6042 P]$ where $P = (F_o^2 + 2 F_c^2)/3$, $N_o = 9445$ observed [$I > 3\sigma(I)$] reflections out of $N = 13960$ unique. One $-C_2H_4-$ group of the crown ether was modelled as disordered over two equally weighted parts, however only one such $-C_2H_4-$ group is shown. C–H hydrogens of the calixarene and crown ether moieties were included as structural invariants.

Crystal structure of [2·37(H₂O)]_{0.5}: C₁₀₂H_{156.5}CrNa_{1.5}O_{83.5}S₁₂, $M = 3190.0$ g mol⁻¹, triclinic, $P\bar{1}$, $a = 17.5737(5)$, $b = 22.5177(7)$, $c = 25.9305(8)$ Å, $\alpha = 111.903(1)$, $\beta = 92.563(1)$, $\gamma = 96.871(1)^\circ$, $V = 9407.6(5)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.13$ g cm⁻³, $F(000) = 3338$, $\mu_{\text{Mo}} = 0.28$ mm⁻¹ (no correction), size: $0.38 \times 0.30 \times 0.21$ mm, $2\theta_{\max} = 40^\circ$, 1934 parameters, final $R_1 = 0.2025$ (observed data), $wR_2 = 0.5042$ [all data, weights $w = 1/[\sigma^2 F_o^2 + 0.1 P^2]$ where $P = (F_o^2 + 2 F_c^2)/3$]. $N_o = 11389$ observed [$I > 3\sigma(I)$] reflections out of $N = 17000$ unique.

Crystal structure of [3·29(H₂O)]_{0.5}: C₁₀₂H_{160.5}Cr₃Na_{1.5}O_{88.5}S₁₂, $M = 3378.05$ g mol⁻¹, triclinic, $P\bar{1}$, $a = 17.8867(6)$, $b = 22.7760(8)$, $c = 26.0857(8)$ Å, $\alpha = 112.015(1)$, $\beta = 93.621(1)$, $\gamma = 96.722(1)^\circ$, $V = 9718.1(6)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.15$ g cm⁻³, $F(000) = 3522$, $\mu_{\text{Mo}} = 0.38$ mm⁻¹, size: $0.35 \times 0.25 \times 0.15$ mm, $2\theta_{\max} = 40^\circ$, 2111 parameters, final $R_1 = 0.2049$ (observed data), $wR_2 = 0.4954$ [all data, weights $w = 1/[\sigma^2 F_o^2 + 0.1 P^2]$ where $P = (F_o^2 + 2 F_c^2)/3$]. $N_o = 11772$ observed [$I > 3\sigma(I)$] reflections out of $N = 17604$ unique.

Note that poor data quality does not allow for the number of water molecules to be established beyond doubt. Data in the range $40^\circ < 2\theta < 50^\circ$ were extremely weak (<15% observed data) for both **2** and **3**, hence all data $2\theta > 40^\circ$ were discarded for refinement purposes. C–H hydrogens of the calixarene and crown ether moieties were included as structural invariants. All non-hydrogen atoms except oxygens associated with disordered dimer and trimer cations for **2** and **3** were refined anisotropically. Crown ether groups for both structures showed signs of disorder hence bond lengths were restrained to be similar. The high R_1 values are a consequence of a high degree of solvation and the extensive disorder and partial occupancy of the cations. It is notable that approximately one third of the crystal volume contains disordered material (cations or water).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-112419, CCDC-112420 and CCDC-112421. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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