Rhodium(III) Aqua Ion Salts of Ambivalent Self Assembled Superanion Capsules

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The self assembled superanionic capsule $[\{Na^+\subset(18\text{-crown-}6)(OH_2)_2\}\subset\{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}]^{7-}$ (X^{7-}) forms a 1:1 crystalline complex with dinuclear $[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ when the cation is treated with sodium *p*-sulfonatocalix[4]arene and 18-crown-6 at pH 2. The overall composition of the crystalline solid is $[Rh_2(\mu\text{-}OH)_2(H_2O)_8][X + 3\,H^+]\cdot 11.5H_2O$. Treatment of a complex mixture of polynuclear rhodium(III) aqua ions in perchloric acid with excess sodium *p*-sulfonatocalix[4]arene and 18-crown-6 at pH 2, results in selective retrieval of the tri- and tetranuclear rhodium(III) species in a single 1:1 co-crystallised phase, isolated as the hydrate salt with overall composition $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}][Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][2\,X + 3\,H^+][Na(H_2O)(ClO_4)]_2\cdot 27H_2O$. The tri- and tetranuclear Rh cations both have a cyclic structure with μ-hydroxide and terminal water ligands. Despite the differences in cation charge and size both complexes show the same arrangement of polynuclear cations and superanions although the trimer/tetramer complex shows additional coordination of a second Na centre by the calixarenes. At pH 0.35 the reaction leads to the selective retrieval of the tetranuclear cation in the complex $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X + \{X - 2\,H_2O\} + 8\,H^+]\cdot 33H_2O$, where a second type of dehydrated superanion is found, where the two sodium bound water molecules have been replaced by O-centres of calixarene sulfonate groups, illustrating the versatile nature of the superanion chemistry.

Introduction

Selective crystallisation of polynuclear metal aqua cations from solutions containing a range of complex polynuclear aqua species has recently been established for a self-assembled superanion capable of taking on different charge to accommodate the surrounding cations.[1,2] The superanion $[\{Na^+\subset(18\text{-crown-}6)(OH_2)_2\}\subset\{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}]^{7-}$, abbreviated hereafter as X^{7-}, is composed of a central sodium ion bound by two *trans* water molecules and an 18-crown-6, and this complex is shrouded by two *p*-sulfonatocalix[4]arenes which hydrogen bond to the inner-sphere water molecules creating a Russian doll-like assembly (Figure 1). Cohesion in the solid state comes from interplay of different supramolecular interactions, notably hydrogen bonding, which includes those for water molecules of crystallisation, electrostatics, π-stacking, and van der Waals. Thus far $[Cr_4(OH)_6(H_2O)_{12}]^{6+}$ and $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ have been selectively retrieved from complex mixtures using this approach.[1,2] Electrostatic repulsion between the calixarenes in the superanions is overcome by the large cations being situated close to the sulfonate groups of adjacent calixarenes. Purified solutions of $[Cr_2(OH)_2(H_2O)_8]^{4+}$ and $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$ can form crystalline complexes with protonated X^{7-}, however the cations are partially occupied with a high degree of dynamic disorder, and cohesion in the solid state is derived instead from extensive π stacking and hydrogen bonding interactions between the superanions.[1] The related though smaller anionic capsule $[H_4(\text{cyclam})\subset\{(p\text{-sulfonatocalix[4]arene})_2\}]^{4-}$ also forms a crystalline complex with $[Cr_2(OH)_2(H_2O)_8]^{4+}$ where the cation is once more ordered and forms close interactions with the sulfonate groups of the superanion.[3] The ionic capsules in this work relate to a recent surge of studies on the self assembly of molecular capsules constructed mainly using hydrogen bonding,[4,5] although hydrophobic interactions and metal coordination mechanisms are also known.[4] Examples of second sphere supramolecular complexation are rare, limited to a metal−cryptate−cavitand assembly[6] as well as second sphere cyclodextrin complexes.[7]

In further exploring this approach we have investigated superanion complexation of polynuclear rhodium(III) aqua cations. Solutions of pure dinuclear rhodium(III) cation $[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ with crown ether and sulfonated calixarene at low pH give a crystalline complex of the superanion in a 1:1 ratio with the dinuclear rhodium(III) cation, with composition $[Rh_2(\mu\text{-}OH)_2(H_2O)_8][X + 3\,H^+]\cdot 11.5H_2O$, **1**. Remarkably, we find that with a mixture of Rh^{III} oligomers treated under the same conditions, the tri- and tetranuclear cations, $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}]^{5+}$ and $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}]^{6+}$, Figure 1, are retrieved from solution in a single 1:1 co-crystallised phase, as a hydrate salt of the self assembled ionic capsule and Na perchlorate with overall composition $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}][Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][2\,X + 3\,H^+][Na(H_2O)(ClO_4)]_2\cdot 27H_2O$, **2**. The ability to co-crystallise two large polynuclear aqua cations in the same solid is without precedent. Moreover, of the two cations, only the trinuclear one has been studied with its existence in solution postulated on the basis of NMR experiments,[8] and there is considerable uncertainty on the nature of higher nuclearity species. Previous work

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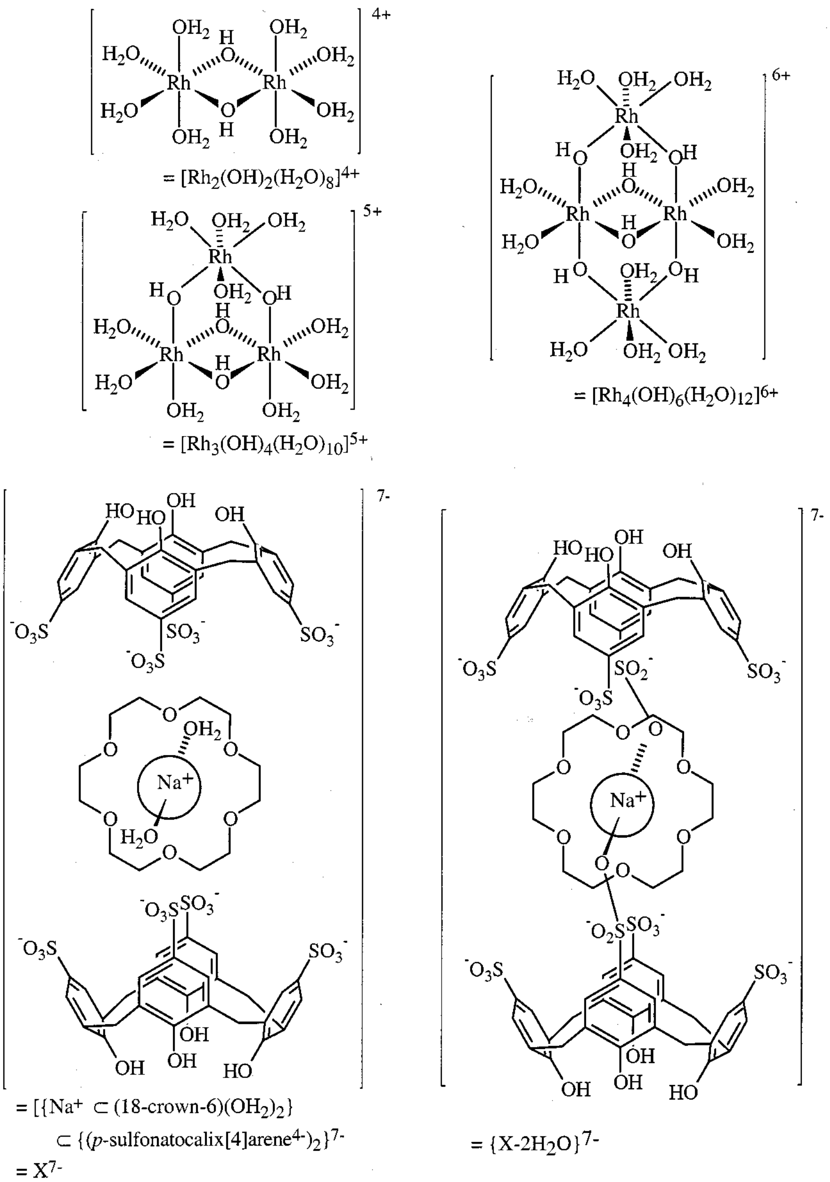

Figure 1. Polynuclear rhodium(III) aqua ions identified as salts of the protonated superanion X^{7-}, and the dehydrated superanion $\{X - 2\,H_2O\}^{7-}$ formed on treating mixtures of the polynuclear species with excess sodium *p*-sulfonatocalix[4]arene and 18-crown-6 at low pH, isolated as hydrates of $[Rh_2(OH)_2(H_2O)_8][X + 3\,H^+]$, $[Rh_3(OH)_4(H_2O)_{10}][Rh_4(OH)_6(H_2O)_{12}][2\,X + 3\,H^+][Na(H_2O)ClO_4]_2$, and $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X + \{X - 2\,H_2O\} + 8\,H^+]$; $X = [\{Na^+(18\text{-crown-6})(OH_2)_2\}\{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}]^{7-}$

authenticating polynuclear rhodium(III) cations in the solid state is restricted to studies on the dinuclear cations,[9,10] with the related mixed Rh^{III}/Cr^{III} dimer also characterised.[11] Oligomeric chromium(III) solutions under the same conditions result in retrieval of the tetranuclear species rather than both the tri- and tetranuclear in the present system. Changes in pH can, however, lead to the selective retrieval of the tetranuclear Rh^{III} species in the complex $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X + \{X - 2\,H_2O\} + 8\,H^+]\cdot 33H_2O$, **3**. Here $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}]^{6+}$ crystallises with the superanion X^{7-} and a radically altered superanion $\{X - 2\,H_2O\}^{7-}$ which is devoid of the two *trans* water molecules with the two calixarenes coordinating directly to the central Na^+ via sulfonate groups, Figure 1, and demonstrates the hitherto unknown ability of the capsule to accommodate large cations by forming different structures, which adds to the previously established versatility inherent in being able to alter its degree of protonation.

Results and Discussion

Yellow crystals of complex **1** formed on the evaporation over several days of an aqueous solution containing $[Rh_2(\mu\text{-}OH)_2(H_2O)_8](ClO_4)_4$, and an excess of sodium *p*-sulfonatocalix[4]arene and 18-crown-6, acidified to pH 2 with aqueous perchloric acid. The solid-state structure was determined from X-ray diffraction data collected at 123(1) K. The complex $Rh_2(\mu\text{-}OH)_2(H_2O)_8][X + 3\,H^+]\cdot 11.5H_2O$, **1** crystallises in a triclinic cell [$a = 13.5248(3)$, $b = 16.7318(4)$, $c = 25.1930(5)$ Å, $\alpha = 105.583(5)$, $\beta = 97.061(4)$, $\gamma = 108.522(5)°$] and the structure was solved in $P\bar{1}$. The structure consists of three major structural components − the superanion capsule and the dinuclear cation in two orientations, as well as water molecules at hydrogen bond distances to these moieties. Three of the total of eight sulfonate groups of the superanion capsule are required to be protonated to achieve overall charge balance. These protons were not located crystallographically and could reside on any of the eight crystallographically distinct sulfonate groups. Surprisingly, the structure of **1** is not isostructural with, or extensively disordered, as in the chromium(III) analogue,[1] where the cations are disordered over several sites within the unit cell. These differences may relate to the larger size of the cation in the present case and/or different polarisation effects.

The $[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ cation in **1** is unexceptional relative to that established for a less-versatile supramolecular approach.[9] The structure of the superanion X^{7-} is similar to those found in the analogous anions in the structures containing the di-, tri-, and tetranuclear chromium(III) cations,[1] and the Keggin ion aluminium(III) cluster, where there is also a calixarene in the crystal lattice that is not part of a capsule.[2] The crown ether within the superanion shows severe dynamic disorder, which is not unusual for crown ether structures.[12]

The extended structure of **1** features a complicated array of hydrogen bonds complemented by additional supramolecular interactions such as electrostatics. There are two types of cation behaviour with both positioned at the periphery of the hydrophilic sulfonate equator of the globular superanion. Numerous hydrogen bonds from the coordinated hydroxides and waters of the cations to the sulfonate groups of the superanion overcome electrostatic repulsion associated with the two sulfonated calixarene molecules, Figure 2. One cation, with the Rh−μ-$(OH)_2$−Rh plane roughly perpendicular to the approximate plane of the crown ether, is located very close to the hydrophilic periphery of two superanions in **1** with O···O hydrogen bond lengths 2.53 to 2.71 Å. The other type of cation sits at the outer edges of four superanions, bridging between them through hydrogen bonding interactions at O···O distances 2.63 to 2.70 Å. The array of hydrogen bonding interactions between the cations and superanions form an infinite two dimensional network, a section of which is shown in Figure 3. In the overall crystal lattice these 2D networks stack in layers through RSO···HOR′ hydrogen bonds (O···O distance 2.71 Å) between calixarenes of different networks. This is quite distinct from the inter-superanion stacking observed in the su-

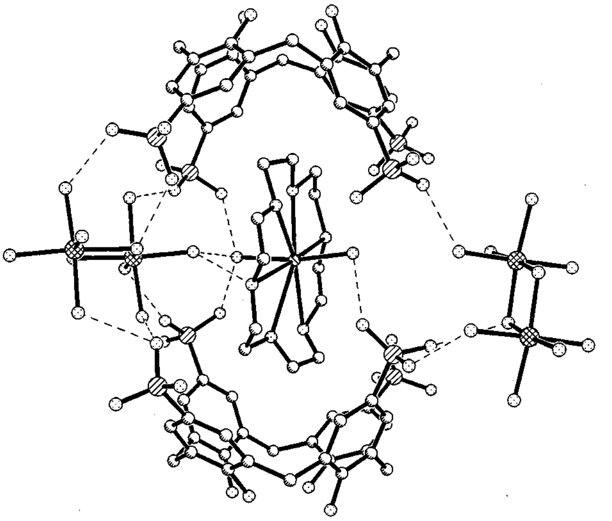

Figure 2. Close contacts between superanion and Rh dinuclear cations in $[Rh_2(\mu\text{-}OH)_2(H_2O)_8][X + 3\,H^+]\cdot 11.5H_2O$ (**1**); dashed lines indicate hydrogen bonds; only one disordered sulfonate group is shown for clarity

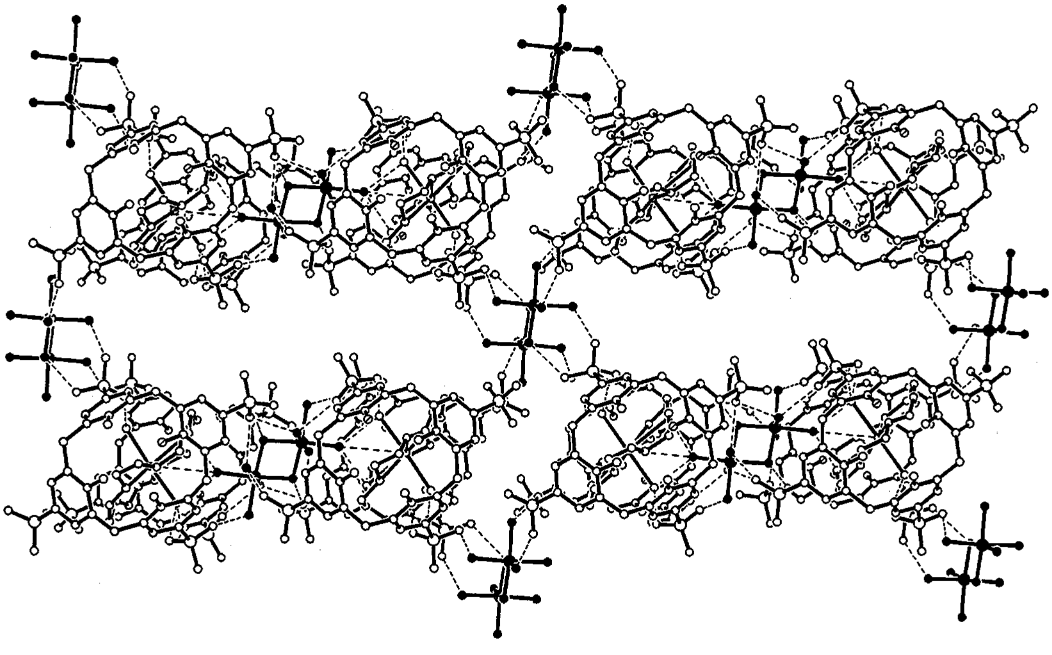

Figure 3. Section of the infinite two dimensional hydrogen bonded network of superanions and dinuclear cations (highlighted in black) of **1**

peranion complexes of $[Cr_2(OH)_2(H_2O)_8]^{4+}$ and $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$ with X^{7-}, where RSO···HOR′ hydrogen bonding was more extensive and complemented by π stacking.

Pale yellow crystals of complex **2** were obtained in a similar manner to **1**, however with a mixture of polynuclear rhodium(III) aqua ions at pH 2 formed by treating aqueous rhodium(III) perchlorate (0.1 M) with sodium hydroxide (1 M) to give a pH 13, then acidifying the resulting solution after 2 hours with perchloric acid. Under such conditions, mononuclear, dinuclear, trinuclear, and higher oligomers are known to exist.[8,9] The solid-state structure was determined from X-ray diffraction data collected at 123(1) K. The complex $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}][Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][2\,X + 3\,H^+][Na(H_2O)(ClO_4)]_2\cdot 27H_2O$, **2** crystallises in a triclinic cell [a = 13.8992(2), b = 17.0191(5), c = 26.6441(7) Å, α = 75.268(3), β = 88.328(5), γ = 68.768(5)°] and the structure was solved in $P\bar{1}$. As for **1** the structure consists of three major structural components − the superanion capsule, trinuclear, and tetranuclear cations as well as sodium perchlorate with the sodium coordinated to the calixarenes, and numerous water molecules. Three of the sixteen sulfonate groups are required to be protonated for charge balance and could reside on any of the eight crystallographically independent sulfonates.

The trinuclear $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}]^{5+}$ of **2** is located close to a crystallographic inversion centre leading to a static disorder of the cation over two positions with some shared oxygen sites having both water and hydroxide character, Figure 4. Such a disorder makes the Rh−O distances somewhat unreliable, however general structural features are unequivocal. The μ-OH bridged cyclic structure of the trinuclear cation is isostructural with that of the chromium(III) analogue,[1] but this is at odds with the assigned linear structure based on ^{103}Rh NMR studies. However, the NMR data showing two resonances in a 1:2 ratio is consistent with the triangular structure.[8] The structure of the tetranuclear $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}]^{6+}$ cation is likewise the same as that for the chromium(III) analogue,[1] and is cyclic with two Rh centres coordinated by two terminal water mo-

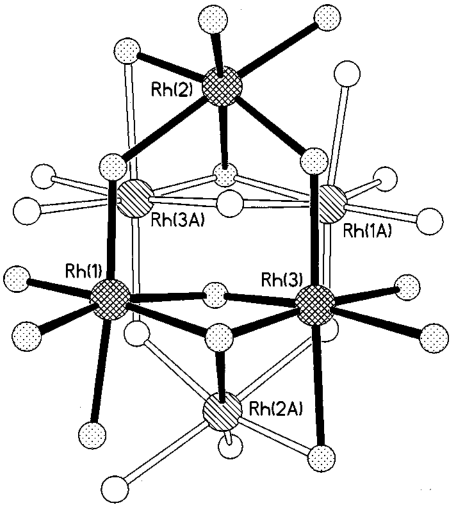

Figure 4. The disordered trinuclear cation $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}]^{5+}$ from the crystal structure of $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}][Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][2\,X + 3\,H^+][Na(H_2O)ClO_4]_2\cdot 27\,H_2O$ (**2**)

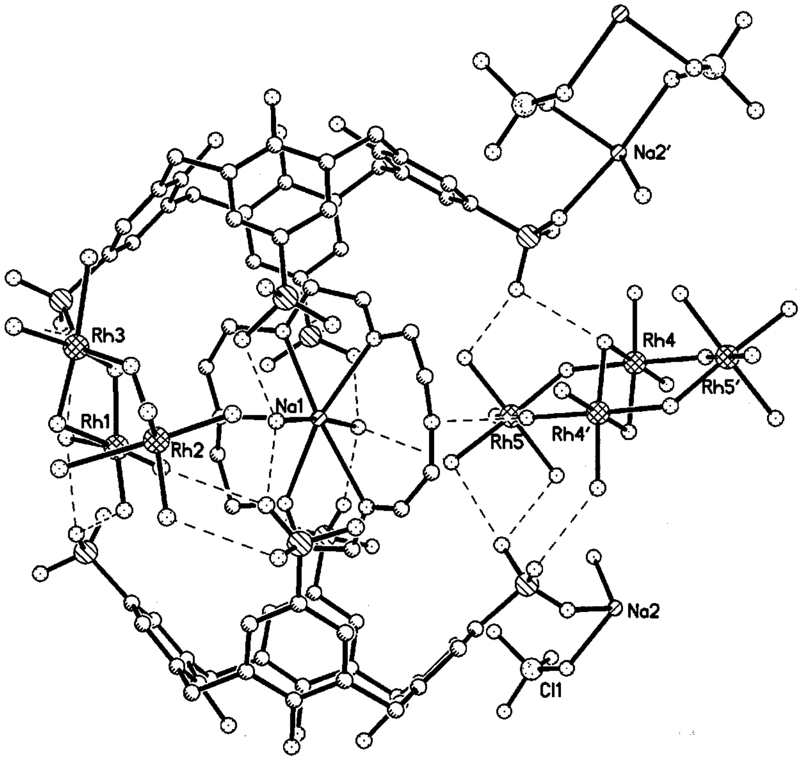

Figure 5. Interactions between the superanion and polynuclear cations in **2** and coordination of Na perchlorate moiety; for the sake of clarity only one position for the disordered sulfonate and trinuclear cation groups are shown

lecules and four bridging hydroxides, the other metal centres coordinated by four terminal water molecules and two bridging hydroxides. Rh−OH$_2$ distances ranges from 2.024(5) to 2.053(6) Å, and Rh−OH distances were from 1.991(5) to 2.007(5) Å.

The structure of the superanion X^{7-} is slightly different to that of **1** and analogous systems,[1,2] with the central Na^+ in **2** coordinating to only five of the six crown ether oxygen atoms at Na−O distances from 2.55(1) to 2.740(9) Å as well as two *trans* water molecules [Na−O distances 2.294(9) and 2.376(7) Å] in a distorted pentagonal bipyramidal geometry, Figure 5. The sixth oxygen is pulled out of the Na^+ coordination sphere by a weak hydrogen bond to a hydroxide of the Rh tetramer at an O···O separation 2.91 Å. The superanion is somewhat tilted when compared with analogous superanions, which appears to be caused by sulfonate groups coordinating to Na^+ centres, Figure 5.

Complexes **1** and **2** both have an overall polynuclear cation to superanion ratio of 1:1, and the packing of these components in their respective crystal lattices is similar, evident in their comparable unit cell parameters. The extended structure of **2**, however, combines two-dimensional hydrogen-bonded networks of polynuclear cations and superanions with metal-coordinated chains running parallel to the *a* axis formed by calixarenes coordinating to Na^+ metal centres. The hydrogen bonded networks are topologically identical to those found in **2**, with the disordered trinuclear $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}]^{5+}$ positioned close to the hydrophilic equator of two superanions forming hydrogen bonds at O···O separations 2.46 to 2.88 Å, and the tetranuclear $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}]^{6+}$ forming hydrogen bonding interactions (O···O separations 2.64 to 2.91 Å) at the outer edges of four superanions. The Na^+ centres within the coordinate chain are six-coordinate, bonding to a terminal water, two bridging perchlorates in a *cis* arrangement, two bridging calixarenes and a terminal calixarene, Figure 6. The bridging calixarenes coordinate to one Na^+ centre through a sulfonate group [Na−O 2.293(7) Å] and to a second Na^+ centre through a hydroxy group [Na−O 2.524(7) Å] of an arene ring adjacent to that of the coordinated sulfonate. Each Na^+ centre has a bridging calixarene coordinating through a sulfonate group and a calixarene bound through a hydroxy group, and these two calixarenes have their cavities oriented in opposite directions and belong to superanions of different 2D hydrogen bonded networks. The terminal calixarene coordinates through a dynamically disordered sulfonate group at distances 2.24(1) and 2.56(2) Å and is in the same orientation as the sulfonate-bound calixarene. Coordination of Na^+ by the sulfonate groups of sulfonated calixarenes has been previously reported;[13] however, this is the first structurally authenticated example of hydroxy coordination, which has been observed for other types of calixarenes.[14] The coordinated Na−perchlorate−calixarene chain is complemented by π-π stacking between arenes of calixarenes in opposite orientations with aromatic centroid−centroid separations ca. 3.9 Å.

Yellow crystals of $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X + \{X - 2\,H_2O\} + 8\,H^+]\cdot 33H_2O$ (**3**) were grown in a similar manner to **2** at pH 0.35, and the solid-state structure was determined from X-ray diffraction data collected at 123(1) K. The complex **3** crystallises in a triclinic cell [a = 17.2141(3), b = 18.1947(3), c = 20.7066(3) Å, α = 88.218(1), β = 77.304(1), γ = 62.429(1) °] and the structure was solved in $P\bar{1}$. The complex **3** has a 1:1:1 ratio of tetranuclear cation, superanion X^{7-}, and dehydrated superanion

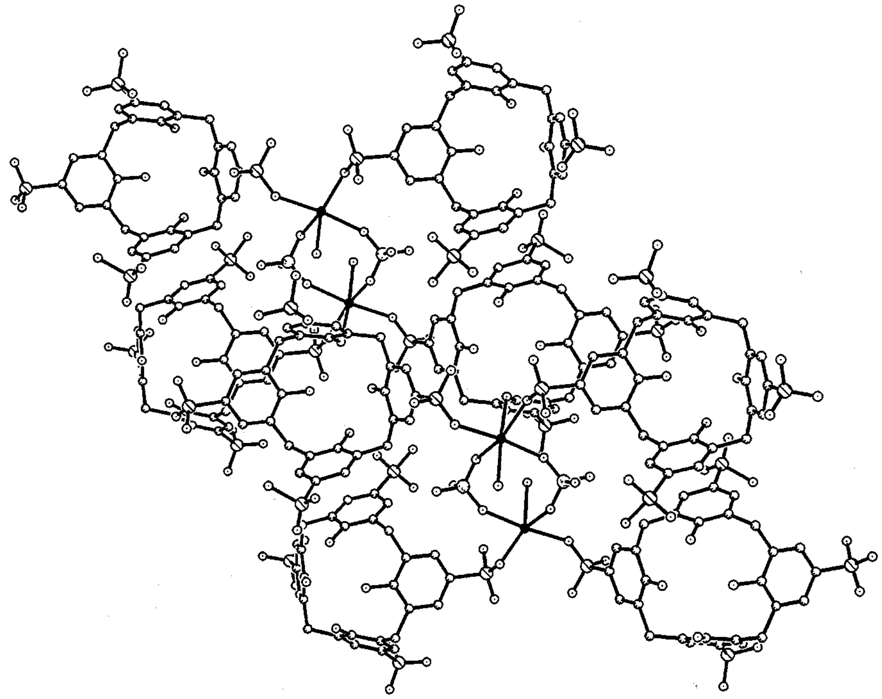

Figure 6. Chain structure of **2** formed by coordination of Na (highlighted in black) by two bridging perchlorates; two bridging calixarenes with sulfonate and hydroxy binding, with terminal water and calixarene ligands also shown

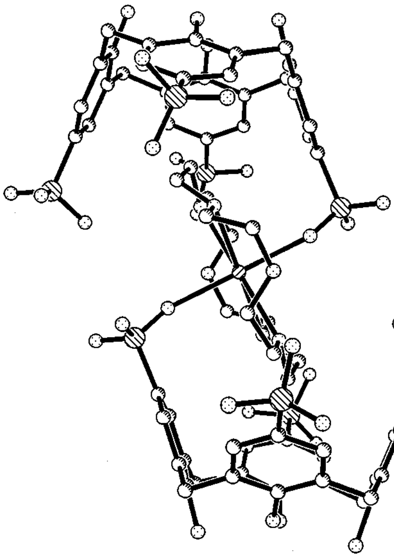

Figure 7. Dehydrated superanion $\{X - 2\,H_2O\}^{7-}$ from the crystal structure of $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X + \{X - 2\,H_2O\} + 8\,H^+]\cdot 33H_2O$ (**3**); displacement of the two calixarene bowls from their usual head-to-head arrangement is clearly visible

$\{X - 2\,H_2O\}^{7-}$ as well as 31 solvent water molecules, and requires a total of eight sulfonate groups to be protonated for charge balance. Not surprisingly given the size of the crystal structure determination, protons were not located crystallographically. The higher ratio of capsules to cations in this structure relative to that of **1** and **2** is consistent with complex formation from a more acidic solution.

The tetranuclear cation is identical to that of **2** and the superanion X^{7-} is similar to those previously reported.[1,2] The structure of the superanion $\{X - 2\,H_2O\}^{7-}$ is skewed considerably from the capsule structure of X^{7-}. The two axial water molecules coordinated to the Na^+ centre in X^{7-} are not present in the dehydrated superanion. Instead the axial coordination positions are occupied by oxygens of sulfonate groups from each of the two calixarene moieties that form the shell of the superanion. The Na−OS distance of 2.319(9) Å requires that one sulfonate group from each of the calixarene subunits is pulled in towards the Na perturbing the usual head-to-head arrangement of calixarenes, leaving the superanion open at each side, Figure 7. The central Na^+ is octahedral and coordinates to four of the six crown ether oxygens [Na−O distances 2.580(8)−2.539(8) Å], with the other two crown oxygens forming hydrogen bonds to solvent water at O···O separation 2.34 Å.

Hydrogen bonding is the dominant interaction present between the different components in complex **3**. Each tetranuclear cation forms hydrogen-bonding interactions to the sulfonate groups of four superanions; two X^{7-} capsules positioned opposite each other across the cation, and two $\{X - 2\,H_2O\}^{7-}$ superanions, at O···O separations of 2.61 to 2.79 Å. Each superanion, whether X^{7-} or $\{X - 2\,H_2O\}^{7-}$, hydrogens bonds to two tetranuclear cations, extending into a two dimensional rectangular grid array shown in Figure 8. Within the crystal lattice the two dimensional grids stack offset to one another and show hydroxy to sulfonate hydrogen bonding and π stacking between calixarenes of adjacent grids, Figure 9. Each superanion forms such interactions to other superanions of both the X^{7-} and $\{X - 2\,H_2O\}^{7-}$ persuasion, at π-π centroid separations 3.53 to 3.78 Å and O···O distances 2.81−3.01 Å. Interestingly, unlike in other examples of π stacking complemented by

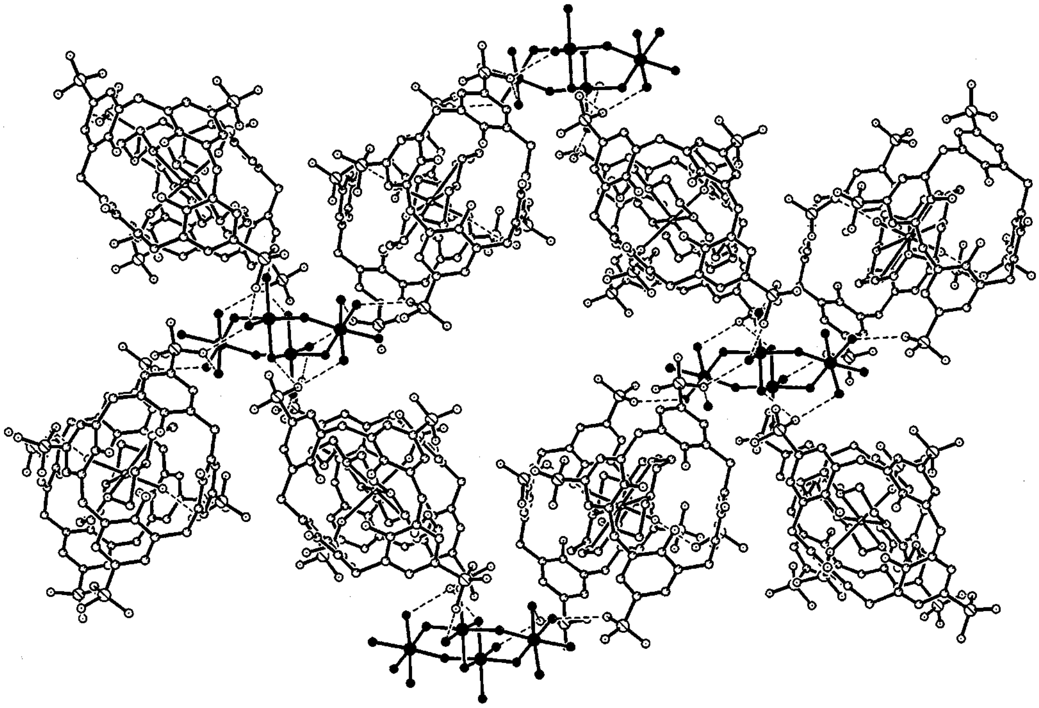

Figure 8. Section of the infinite hydrogen bonded grid structure formed by tetranuclear cations $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}]^{6+}$ and superanions X^{7-} and $\{X - 2\,H_2O\}^{7-}$ in **3**; for the sake of clarity only one position for the disordered sulfonate in the X^{7-} superanion is shown

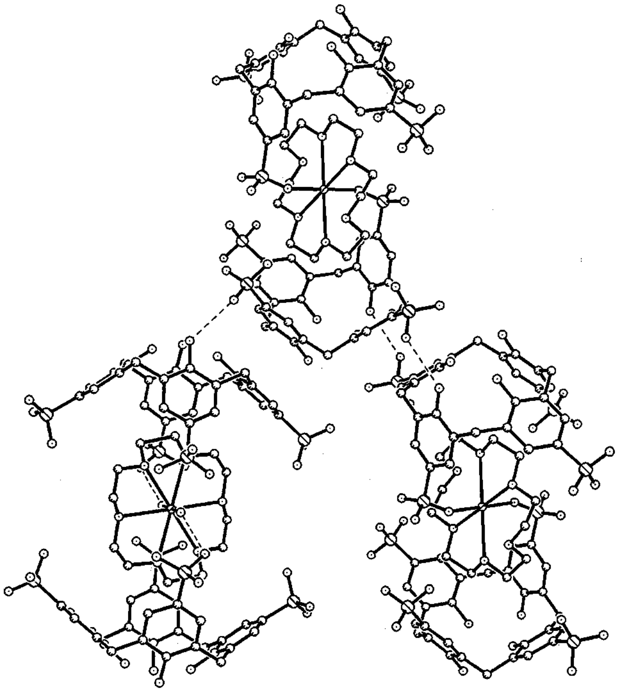

Figure 9. Hydrogen bonding and π-π stacking interactions between superanions of **3**; for the sake of clarity only one position for the disordered sulfonate in the X^{7-} superanion is shown

RSO···HOR′ hydrogen bonding where both interactions occur in the one pair of HO−aryl−SO_3 moieties, the sulfonate groups are oriented such that they accept a hydrogen bond from a hydroxy group adjacent to the aromatic ring involved in the π stack. Spaces within the lattice are occupied by disordered solvent water molecules.

Previously established types of superanions have demonstrated an ability to exist in various states of negative charge, and to either include or exclude Na^+ from the inner core of the capsule depending on reaction conditions. Now it is also seen that the nature of the coordination sphere of the capsule can be altered by a slight variation in reaction conditions. The ambivalent nature of the superanion assembly, either X^{7-} or $\{X - 2\,H_2O\}^{7-}$ in their various protonated forms, is noteworthy, and may be a consequence of crystal packing. The nature of the compounds present in solution is yet to be realised, and has proved a difficult task for all such systems to date.

Conclusions

The ability of the superanion to take on different charges via protonation of the terminal sulfonate is evident in the current structures, and the work further highlights its versatility in complexing two disparate polynuclear species both in charge, size, and shape, in the same lattice, which is without precedent in polynuclear aqua cation chemistry. The complexation of mixed Rh^{III} and Cr^{III} clusters is also likely to lead to some selectivity and for this system only the dinuclear species has been authenticated.[11] The ambivalent nature of the capsule X^{7-} versus $\{X - 2\,H_2O\}^{7-}$ is surprising and highlights the complexity in studying these systems introducing another structural assembly parameter. Overall, our approach to crystallising large cations is indeed more general than initially realised, and the concept of forming capsules by using large cations to overcome the electrostatic repulsion between the two calixarenes has implications in forming capsules with a large array of different organic and inorganic substrates in the core.

Experimental Section

Preparation of 1−3: A mixture of monomeric and oligomeric Rh^{III} cations was produced by treating aqueous rhodium(III) perchlorate (0.1 M) with sodium hydroxide (1 M) to pH 13, standing for 2 hours then acidifying with 60% perchloric acid to approximate pH 2. Solutions containing pure $[Rh_2(\mu\text{-}OH)_2(H_2O)_8](ClO_4)_4$ in aqueous acid were obtained by chromatographic techniques.[8] Crystals of $[Rh_2(\mu\text{-}OH)_2(H_2O)_8][X + 3\,H^+]\cdot 11.5\,H_2O$ (**1**) were obtained by adding an excess of sodium *p*-sulfonatocalix[4]arene and 18-crown-6 to such a solution, adjusting the pH to 2 with aqueous perchloric acid and standing the solution uncapped in ambient conditions for several days. Crystals of $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}][Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][2\,X + 3\,H^+][Na(H_2O)(ClO_4)]_2\cdot 27\,H_2O$ **2** were obtained in a similar fashion using the unpurified mixture of Rh^{III} cations in acid. Conditions for the formation and crystallisation of $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X + \{X - 2\,H_2O\} + 8\,H^+]\cdot 33\,H_2O$ **3** were identical to those of **2** except with the initial pH less than 1. Reliable elemental analytical data could not be obtained due to the large proportion of solvent water present in the crystalline complexes.

Crystal Structure Determination: All crystals were sensitive to loss of solvent and were mounted on a glass capillary under oil. Data for **1**−**3** were collected at 123(1) K on an Enraf−Nonius KappaCCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å). Data were corrected for Lorentzian and polarisation effects but not absorption. The structures were solved by direct methods (SHELXS-97) and refined with either a full matrix or blocked-matrix least-squares refinement on F^2 (SHELXL-97). Unless otherwise indicated all non-hydrogen atoms were refined anisotropically. Results of the structure refinements are summarised in Table 1, while details of the treatment of disorder and hydrogens are given below.

$[Rh_2(\mu\text{-}OH)_2(H_2O)_8][X + 3\,H^+]\cdot 11.5H_2O$ (1): One sulfonate group and the crown ether showed dynamic disorder. The sulfonate group was modelled as having O sites disordered over two positions with occupancies 0.7 and 0.3. The behaviour of the crown ether moiety suggested a severe dynamic disorder, probably rotation about the $H_2O-Na-OH_2$ axis, that could not be adequately modelled. The eventual model used has all carbon positions refined with a common set of displacement parameters and all oxygen positions refined with a common set of displacement parameters, although it is recognised that some positions may have mixed C/O character. The higher than usual displacement parameters and some nonsensical bond lengths and angles are a consequence of this disorder. There were a number of disordered water molecules with low occupancy some of which were refined isotropically and C−H hydrogen atoms on the calixarenes were included at calculated positions with a riding refinement.

Table 1. Crystal structure data and details of structure refinement for **1** to **3**

	1	**2**	**3**
Formula	$C_{68}H_{112}NaO_{61.5}Rh_2S_8$	$C_{136}H_{251}Cl_2Na_4O_{149}Rh_7S_{16}$	$C_{136}H_{236}Na_2O_{129}Rh_4S_{16}$
M_r [g mol^{-1}]	2398.87	5666.56	4905.85
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.5248(3)	13.8992(2)	17.2141(3)
b [Å]	16.7318(4)	17.0191(5)	18.1947(3)
c [Å]	25.1930(5)	26.6441(7)	20.7066(3)
α [°]	105.583(5)	75.268(3)	88.218(1)
β [°]	97.061(4)	88.328(5)	77.304(1)
γ [°]	108.522(5)	68.768	62.429(1)
V [Å^3]	5069.8(2)	5667.9(2)	5547.4(2)
Z	2	1	1
$\rho_{calcd.}$ [g cm^{-1}]	1.571	1.660	1.457
μ [mm^{-1}]	0.600	0.791	0.55
Refinement type	Full matrix	Block matrix	Full matrix
2θ max [°]	56.6	56.6	55.0
Reflns collected	32085	61992	54268
Unique reflns	22105	26802	25421
R_{int}	0.038	0.061	0.059
Obs. refln $I > 2\sigma(I)$	15966	14320	13875
Restraints	0	0	18
Parameters	1257	1546	1204
R_1 (obs data)	0.0894	0.1151	0.1299
wR_2 (all data)	0.2622	0.3092	0.2149
S	1.036	1.718	1.340

$[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}][Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][2\,X + 3\,H^+][Na(H_2O)(ClO_4)]_2\cdot 27H_2O$ (2): The trinuclear $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}]$ was located over an inversion centre resulting in a static disorder over two positions each at 0.5 occupancy with some shared oxygen sites at full occupancy. A disordered sulfonate was modelled with O sites over two positions at 0.5 occupancies. There were a number of disordered water molecules with low occupancy some of which were refined isotropically and C−H hydrogen atoms on the calixarenes and crown ether were included at calculated positions with a riding refinement.

$[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X + \{X - 2\,H_2O\} + 8\,H^+]\cdot 33H_2O$ (3): The behaviour of the crown ether in the X^{7-} capsule suggested dynamic disorder, and was modelled in a similar manner to the disordered crown in **1**. Two of the sulfonate groups on the X^{7-} capsule also displayed dynamic disorder. The oxygen atoms of these sulfonates were refined isotropically, with the oxygen positions split over two sites at 0.7:0.3 occupancies for one of the disordered sulfonate groups, and S−O bond lengths, and O···O non-bond lengths restrained to maintain a chemically reasonable model. Disordered water molecules were also refined isotropically and C−H hydrogen atoms on the calixarenes and crown ethers were included at calculated positions with a riding refinement.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138364, (**1**), CCDC-138365, (**2**) and CCDC-138366, (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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