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Selective isolation of Keggin ions using self-assembled superanion capsules †

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Crystals of composition $[Al_{13}O_4(OH)_{24}(H_2O)_{12}][Na(18\text{-crown-6})(H_2O)_2L_2(H^+)_w]_{0.5}{}^{x-}[\{L(H^+)_y\}]^{z-}\cdot 29H_2O$ **1**, where $x + z = 7$ and L = *p*-sulfonatocalix[4]arene, were obtained from an aqueous solution containing monomeric and oligomeric aluminium species, Na_4L and 18-crown-6. The crystal structure features three distinct elements: the cationic Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, an anionic capsule $[Na(18\text{-crown-6})(H_2O)_2L_2(H^+)_w]^{x-}$ and a water bearing calixarene. The anionic capsule comprises a central sodium ion bound by 18-crown-6 and two *trans* water molecules, which is in turn encapsulated by two *p*-sulfonatocalix[4]arene molecules in a head-to-head arrangement. The different components are held together in the solid state by an intricate pattern of hydrogen bonds, complemented by other supramolecular interactions such as π–π stacking.

Introduction

The importance of the formation of polynuclear metal aqua ions[1] and the interaction of water with aromatic moieties in biological systems[2] has been well documented. Recent advances in supramolecular chemistry have allowed the development of a new type of self-assembled water soluble superanion capable of altering its degree of protonation and geometrical configuration to accommodate the charges and sizes of a broad range of polynuclear aqua cations.[3] This globular like superanion or ionic capsule with axial symmetry consists of two sulfonated calix[4]arene molecules which encapsulate a central sodium cation bound by a crown ether and two *trans*-water molecules. A range of cohesive supramolecular interactions are important in the assembly of the capsule in the solid state including hydrogen bonding, electrostatic, π stacking, and van der Waals. Previous studies on the self assembly of molecular capsules have largely focussed on hydrogen bonding[4–14] although hydrophobic interactions and metal co-ordination mechanisms are also known.[4]

The ability of the superanion to interact with a range of polynuclear aqua cations with different charge, size and shape in a common structural moiety has been demonstrated by its cocrystallisation with a number of novel polynuclear chromium(III) hydrolysis products: $[Cr_2(OH)_2(H_2O)_8]^{4+}$, $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$ and $[Cr_4(OH)_6(H_2O)_{12}]^{6+}$, in some cases allowing structural authentication for the first time.[3] Furthermore, it is possible selectively to bind cations to the superanion from solutions containing oligomeric mixtures according to the size and shape of the cation, which has relevance in the field of separation science. This technology has been applied in the present study selectively to isolate and characterise structurally a labile main group metal hydrolytic Keggin ion, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, which has been the subject of numerous ^{27}Al NMR studies[15–19] and a preliminary X-ray structural investigation.[20] The superanion is found to crystallise with the Keggin ion and a water-bearing calixarene similar to a hydrated calix[4]arene sulfonate which exhibits aromatic π-electron hydrogen bonding.[2]

Experimental

Synthesis

An aqueous solution of $AlCl_3$ (0.2 M) was treated with NaOH to pH 4.5. Previous ^{27}Al NMR studies have revealed that significant quantities of $[Al(H_2O)_6]^{3+}$ and $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ exist at this pH along with minor amounts of higher oligomers, the relative quantities of which vary with aging.[15] Treatment of the oligomeric aluminium(III) mixture (1 mL) with aqueous solutions of Na_4L (L = *p*-sulfonatocalix[4]arene) (1 mL, 0.03 M) and 18-crown-6 (1 mL, 0.003 M) results in the selective binding/spontaneous self assembly of a complex crystalline supramolecular system of composition $[Al_{13}O_4(OH)_{24}(H_2O)_{12}][Na(18\text{-crown-6})(H_2O)_2L_2(H^+)_w]_{0.5}{}^{x-}[L(H^+)_y]^{z-}\cdot 29H_2O$ **1**, where $x + z = 7$. An excess of crown ether over calixarene was used and the overall yield was 65% with calixarene as the limiting reagent.

X-Ray crystallography

Colourless needle-like crystals of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}][Na(18\text{-crown-6})(H_2O)_2L_2(H^+)_w]_{0.5}{}^{x-}[\{L(H^+)_y\}^{x-}]\cdot 29H_2O$ **1** suitable for X-ray diffraction experiments were grown from aqueous solution in one week. Data were collected at 123(1) K on an Enraf-Nonius KappaCCD diffractometer with Mo-Kα radiation. The structure was solved by direct methods (SHELXS 97) and refined with blocked-matrix least squares on F^2 (SHELXL 97).[21] All non-hydrogen atoms were refined anisotropically and hydrogen atoms on the calixarenes and crown ether included at calculated positions with a riding refinement. There were a large number of solvent water molecules within the crystal lattice some of which were refined as disordered over two sites.

Crystal data. $C_{62}H_{167}Al_{13}Na_{0.5}O_{105}S_8$, $M_r = 3211.68$, triclinic, space group $P\bar{1}$, $a = 17.5261(5)$, $b = 20.2736(6)$, $c = 21.7395(6)$ Å, $\alpha = 117.477(1)$, $\beta = 109.025(1)$, $\gamma = 91.382(1)°$, $U = 6340.5(3)$ Å^3, $Z = 2$, $D_c = 1.682$ g mol^{-3}, $\mu = 0.360$ mm^{-1} (no correction), $2\theta_{max} = 50°$, 40508 data collected, 21506 unique ($R_{int} = 0.038$), 1735 parameters, no restraints, $R1 = 0.0928$ (14135 data $I > 2\sigma(I)$), $wR2 = 0.27721$ (all data), $S = 1.029$.

CCDC reference number 186/1628.

See http://www.rsc.org/suppdata/dt/1999/3639/ for crystallographic files in .cif format.

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3639/

Results and discussion

The solid state structure of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}][Na(18\text{-crown-}6)(H_2O)_2L_2(H^+)_w]_{0.5}[L(H^+)_y]\cdot 29H_2O$ **1** was determined from X-ray diffraction data collected at 123(1) K. The crystal structure consists of three major structural components, the Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, the ionic capsule $[\{Na^+(18\text{-crown-}6)(H_2O)_2\}\{L_2(H^+)_w\}]^{x-}$, a calixarene containing water $[L(H_2O)_3(H^+)_y]^{z-}$, where $x + z = 7$, and numerous water molecules at hydrogen bonding distances to the other components. One sulfonate group of each of the calixarenes of the ionic capsule or one sulfonate group of the other calixarene is required to be protonated to achieve overall charge balance. This proton was not located crystallographically and could reside on any of the eight distinct sulfonates. The structure is held together by an intricate and complicated array of hydrogen bonds complemented by additional supramolecular interactions such as π stacking and electrostatics.

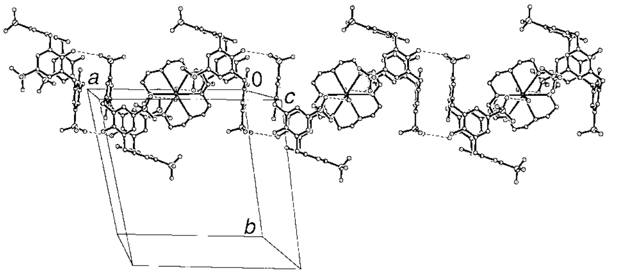


Fig. 1 Chains of the superanion $[\{Na^+(18\text{-crown-}6)(H_2O)_2\}\{L_2(H^+)_w\}]^{x-}$ along the *a* direction. Superanions consist of a Na(crown ether)$(H_2O)_2$ encapsulated by two sulfonated calix[4]arenes. Infinite hydrogen bonded chains of the superanion form through intercalixarene O–H ··· O–S interactions at O ··· O separation 2.80 Å.

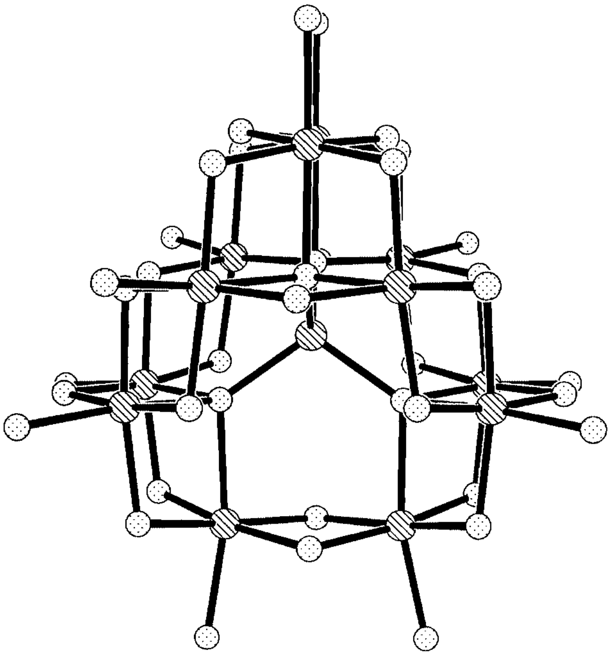
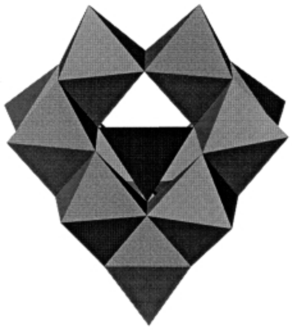
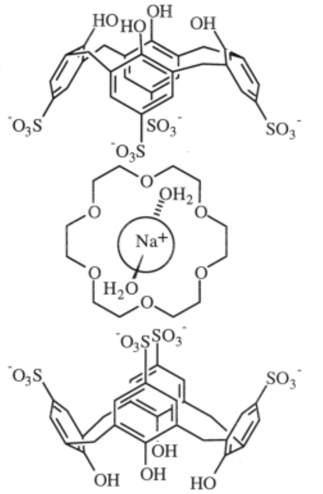
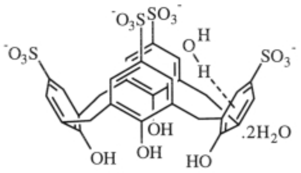


Fig. 2 The Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ from the crystal structure of **1**. The structure consists of twelve AlO_6 octahedra and a central four-co-ordinate aluminium cluster, AlO_4.



$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$





The structure of the superanion consists of a central sodium ion core bound to an 18-crown-6 through the six oxygen centres, and two *trans*-water molecules, so that the sodium ions are eight co-ordinate in a bicapped hexagon array. This cation is encapsulated by two sulfonated calixarenes. The supramolecular assembly is stabilised by hydrogen bonds between the two water molecules attached to the sodium centres, and the sulfonate groups, and the hydrophobic complementarity of the peripheral of the crown ether with the cavity of the calixarenes. There is also the shape complementarity of crown ether and calixarene supramolecular synthons which is achieved by two opposite phenol rings of both calixarenes being splayed apart. The dihedral angles between the plane of these rings and the plane of the four phenolic oxygen atoms are 104.2 and 108.7°. Geometrical constraints necessitate the other pairs of phenol rings be directed in, corresponding dihedral angles being 140.2 and 156.1°. The associated sulfonato groups are hydrogen bonded to the two *trans*-water molecules attached to the sodium, and the peripheral of the crown ether faces the phenol rings which are splayed apart (Fig. 1). The calixarene with the water in the cavity has a less distorted bowl shape with the corresponding dihedral angles at 113.3, 120.6, 125.6 and 136.1°.

The superanions run in chains along the *a* direction of the crystal structure (Fig. 1). These chains are formed through O–H ··· O–S intercalixarene hydrogen bonds at an O ··· O distance of 2.80 Å, complemented by π stacking with a π ··· π ring centroid separation of 3.47 Å. This arrangement of superanions is distinct to those found in previously reported examples containing oligomeric chromium(III) cations.[3]

The aluminium(III) Keggin ion (Fig. 2) is a Al_{13} cluster made up of discrete aluminium–oxygen groups where twelve AlO_6 octahedra are joined together by means of common edges and the central tetrahedron of oxygen atoms contains the four-co-ordinate aluminium atom, AlO_4, $Al_{central}$–O 1.815(5)–1.842(5), Al–OH 1.829(5)–1.891(5) and Al–OH_2 1.917(6)–1.961(6) Å. The structure in the present study is consistent with that reported previously by Johansson[20] who used hydrolysed $AlCl_3$ to obtain crystals of the Al_{13} species as sulfate or selenate salts. The Keggin ions run in hydrogen bonded chains along the *b* direction (Fig. 3) perpendicular to the hydrogen bonded chains of superanions. There are six extremely close inter-Keggin interactions at O ··· O separations ranging from 2.70 to 2.85 Å.

Aromatic π hydrogen bonding to water has been reported for the complex $Na_4L\cdot 13.5H_2O$.[2] In that example a water molecule is imbedded within the bowl of the calixarene molecule at O ··· π centroid distances 3.16, 4.19, 3.19 and 4.08 Å. The

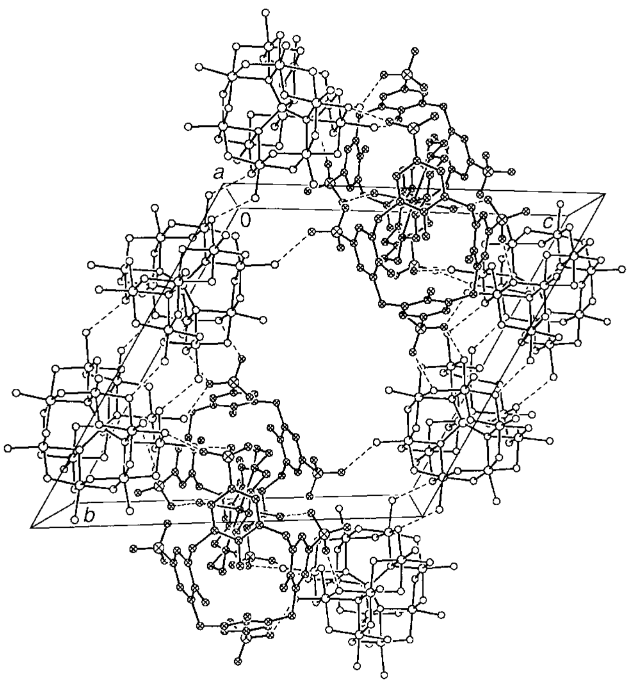


Fig. 3 Interplay of Keggin ions and superanions (shown cross-hatched) within $[Al_{13}O_4(OH)_{24}(H_2O)_{12}][Na(18\text{-crown-6})(H_2O)_2L_2(H^+)_w]_{0.5}^{x-}[L(H^+)_y]^{z-}\cdot 29H_2O$, **1**, $x + z = 7$, viewed down the *a* axis. The Keggin ions $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ run in infinite hydrogen bonded chains along the *b* direction with inter-Keggin O···O separations ranging from 2.70 to 2.85 Å. Solvent water and the water-bearing calix[4]arene are not shown for clarity and occupy the apparent spaces within the cell.

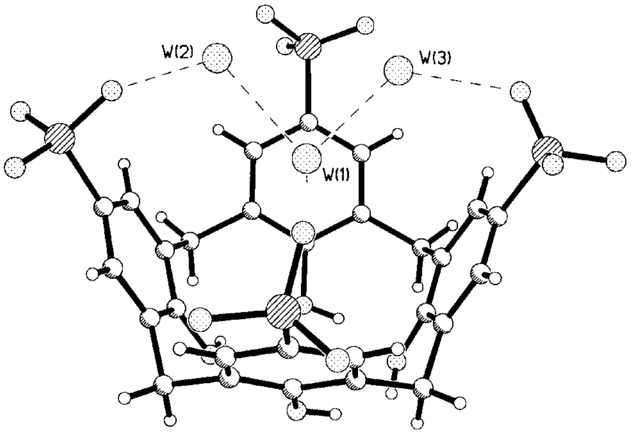
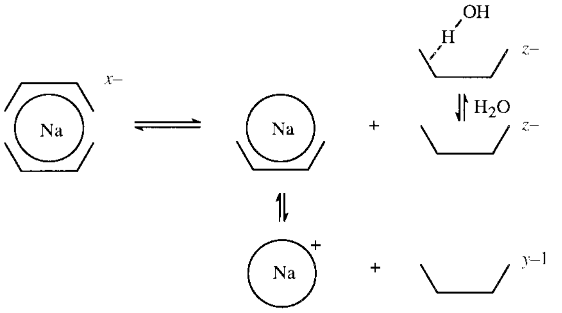


Fig. 4 Sulfonated calix[4]arene as a host for water molecules. Encapsulated water W1 and hydrogen bonded waters W2 and W3. O···O contacts: W1···W2 2.76, W1···W3 2.70 Å. The closest W1···π interaction is shown at O···π centroid distance 3.48 Å.

closest interactions are consistent with O–H···π hydrogen bonding, with hydrogens directed at opposite aromatic rings within the calixarene. The imbedded water molecule showed additional hydrogen bonding interactions to two other water molecules. The present calixarene–water complex species is remarkably similar. One water molecules sits within the calixarene bowl and hydrogen bonds to two additional water molecules located around the sulfonated rim of the calixarene at O···O distances 2.76 and 2.70 Å. These waters each form a further hydrogen bond to the sulfonate groups at O···O distances 2.71 and 2.76 Å (Fig. 4). The O···π centroid distances are on average approximately 10% longer than for $Na_4L\cdot 13.5H_2O$ at 3.48, 3.83, 4.78 and 4.00 Å. In contrast to $Na_4L\cdot 13.5H_2O$ the closest interactions are to adjacent aromatic rings within the calixarene. *Ab initio* calculations of a $C_6H_6\cdot H_2O$ complex gave an optimised O···π centroid distance of ≈3.4 Å,[22] marginally shorter than the present closest contact.

Numerous hydrogen bonding interactions occur between the cation, the superanion, the water-bearing calixarene and the 52 additional water molecules within the unit cell. The Keggin ion to superanion ratio is 2 : 1, with each Keggin ion hydrogen bonding to three anionic capsules and one water-bearing calixarene, while each superanion hydrogen bonds to six Keggin ions. The Keggin ions are positioned at both the periphery of the hydrophilic sulfonate equator of the globular superanion, and at the outer edges of the sulfonates, thus overcoming electrostatic repulsion arising from the close proximity of the sulfonate groups associated with the two sulfonated calixarene molecules. Given that the Keggin ions and superanions also form perpendicular chains, a complicated 3-D hydrogen bonded network of Keggin ions and superanionic capsules is formed (Fig. 3). The water-bearing calixarenes and water molecules fit into voids left by this network.

The presence of both the superanion and a calixarene in the solid state structure implies that a delicately balanced equilibrium between the superanion and water containing calixarene may exist in solution, as shown in Scheme 1. Indeed, the outcome of the supramolecular interplay in the solid state, with crown ether or water in the cavity of each calixarene even in the presence of an excess of crown ether, may be governed by crystal packing forces.



Scheme 1 Equilibrium between the superanion and a calixarene containing a π-electron hydrogen bonded water molecule.

The ability of the superanion $[\{Na^+(18\text{-crown-6})(H_2O)_2\}\{L_2(H^+)_w\}]^{x-}$ to vary its charge *via* protonation of the terminal sulfonate groups has been further demonstrated by its ability to accommodate the substitutionally labile aluminium(III) Keggin ion. This contrasts with the previous study on salts of the superanion with the inert chromium(III) oligomers, dimer (+4), trimer (+5) and tetramer (+6),[3] and further highlights the versatility of this superanion to crystallise polynuclear cations over a broad range of size, charge and reactivity. Moreover, the ability of the crown ether and calixarene to assemble into the capsule and the calixarene to assemble with water in the cavity suggests an even broader scope for supramolecular chemistry involving large and complicated metal cations, and also organic cations.

Acknowledgements

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