Cyclam as a supramolecular synthon: infinite stacked arrays to encapsulation in superanions

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Cyclam crystallised from $CHCl_3$–hexane gives infinite, hydrogen bonded assembled columns; in acidic aqueous media (pH 2) in the presence of sodium *p*-sulfonatocalix[4]arene and the dichromium(III) aqua ion, the superanion or ionic capsule $[[H_4(cyclam)]^{4+} \subset \{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}]^{4-}$ crystallises as the salt of $[Cr_2(OH)_2(H_2O)_8]^{4+}$.

Cyclam (1,4,8,11-tetraazacyclotetradecane) is a traditional macrocyclic ligand in metal ion chemistry.[1] It can be di- or tetra-protonated at low pH to form cationic macrocycles. The tetra-protonated form $[H_4(cyclam)]^{4+}$ adopts an *exodentate* conformation[2] while the di-protonated $[H_2(cyclam)]^{2+}$ and neutral molecule adopt an *endodentate* conformation.[3,4] The neutral molecule has four nitrogen centres capable of hydrogen bonding, as donor and/or acceptor groups, and in this regard its potential in supramolecular chemistry, at least where one of the modes in intermolecular interplay involves hydrogen bonding, is yet to be realised. Both the di- and tetra-protonated forms, on the other hand, have been used as templates in crystal engineering studies, forming polymeric arrays with a variety of anions.[2,3] In exploring this chemistry we have discovered two remarkable, disparate, hydrogen bonding arrays. One of these is the crystallisation of solvent free, pure cyclam from $CHCl_3$–hexane solutions.

The other hydrogen bonding array is associated with the formation of a new ionic capsule where the $[H_4(cyclam)]^{4+}$ is shrouded by two *p*-sulfonatocalix[4]arenes, *viz* $[[H_4(cyclam)]^{4+} \subset \{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}]^{4-}$ (Θ^{4-}), isolated as the salt of the dichromium(III) cation $[Cr_2(OH)_2(H_2O)_8]^{4+}$. The bowl-shaped, highly charged and water soluble *p*-sulfonatocalixarenes, usually used as their sodium salts, show remarkable inclusion properties for ionic guests and neutral molecules, for both calix[4 and 5]arenes.[5] As to the ionic capsule reported, we note that these classes of compounds have only recently been established, but with a metal crown ether complex in the centre of the capsule, $[\{Na^+ \subset (18\text{-crown-6})(OH_2)_2\} \subset \{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}]^{7-}$, which is effective in crystallising, in some cases selectively, the polynuclear cations $[M_2(OH)_2(H_2O)_8]^{4+}$, $[M_3(OH)_4(H_2O)_{10}]^{5+}$ and $[M_4(OH)_6(H_2O)_{12}]^{6+}$ (M = Cr or Rh), and $[Al_{13}O_4(OH)_{12}(OH)_{24}(H_2O)_{12}]^{7+}$.[6] Ionic capsules relate to other contemporary studies on self-assembly of neutral molecular capsules,[7] as does the formation of a 1:1 crown ether to calixarene perched structure with lanthanum(III) in the crown ether, $[\{Ln^{3+} \subset (18\text{-crown-6})(OH_2)_3\} \cap \{(p\text{-sulfonatocalix[4]arene}^{4-} + 2H^+)\}]^+$.[8] The ionic capsule is without precedence, and its ability to crystallise as a dichromium(III) aqua cation suggests it has potential in forming complexes of a wide range of large cationic species, with ultimate applications in separation science. A key feature of the ionic capsules is the complementarity of curvature of the cyclam with the calixarene, albeit with some geometrical preorganisational requirements.

Complex $[Cr_2(OH)_2(H_2O)_8]^{4+}\Theta^{4-}$ crystallised from a solution of cyclam, sodium *p*-sulfonatocalix[4]arene, and the perchlorate salt of the dichromium(III) cation, with the pH adjusted to 2 using perchloric acid (Scheme 1).† This is the only example of an ionic capsule where the charge on the superanion matches that required by the polynuclear cation, without the need to invoke some degree of protonation of the superanion, unlike for complexes involving $[\{Na^+ \subset (18\text{-crown-6})(OH_2)_2\} \subset \{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}]^{7-}$, which can adjust the degree of protonation depending on the polynuclear cation.

Crystals suitable for X-ray diffraction studies of cyclam and $[Cr_2(OH)_2(H_2O)_8]^{4+}\Theta^{4-}.6(H_2O)$‡ deposited over several days. Both crystallise in $P\bar{1}$ systems with the two independent cyclams residing over centres of symmetry (Fig. 1), or the ionic capsule and cation residing over inversion centres (Fig. 2). Cyclam has been reported to have an *endodentate* conformation[4] although a detailed structure is not available.[9] Cyclam (Fig. 1) has two opposite NH groups in the plane of and directed into the centre of the macrocycle, which form intramolecular hydrogen bonds across the 1,3-diamine groups at N–H⋯N distances of 2.243 and 2.273 Å (corresponding N⋯N 2.934 and 2.948 Å) and angles at the hydrogen of 135.7 and 133.1°. These are slightly longer interactions than the intramolecular hydrogen bonding observed for $[H_2(cyclam)]^{2+}$.[3] The remaining two N–H groups are directed away from the macrocycle and form
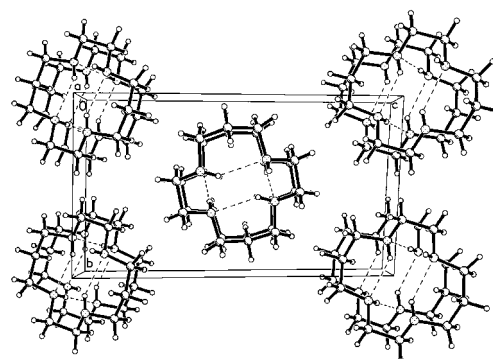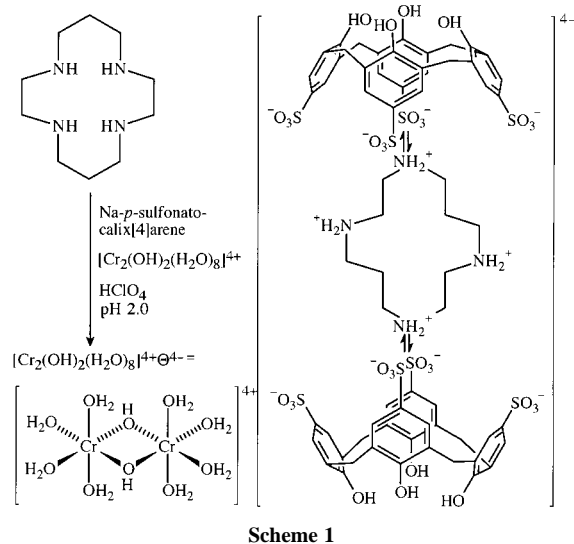

Scheme 1

Fig. 1 Packing diagram for cyclam showing the intermolecular hydrogen bonded columnar arrays and intramolecular hydrogen bonding (hydrogen bonds indicated by dashed lines).
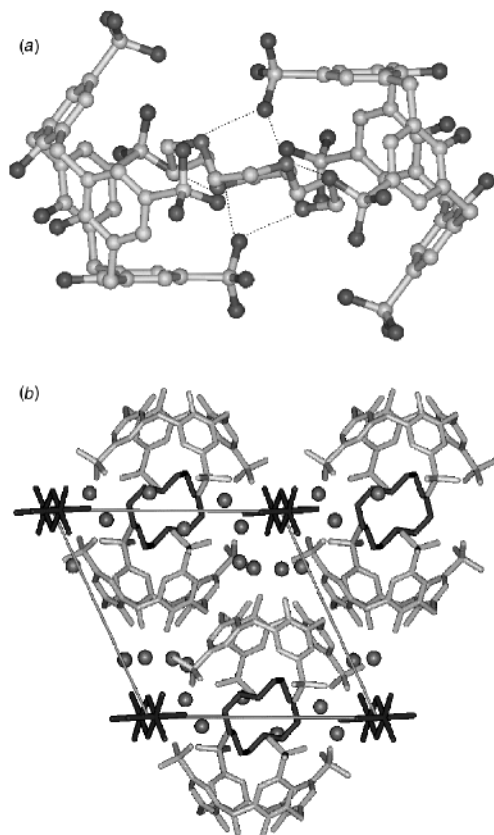
Fig. 2 Projection of (*a*) the superanion [[H$_4$(cyclam)]$^{4+}$ $\subset$ {(*p*-sulfonatocalix[4]arene^{4-})$_2$}]$^{4-}$ (Θ^{4-}), hydrogen atoms have been removed for clarity and implied hydrogen-bonding interactions are represented by dashed lines, and (*b*) unit cell and packing in [Cr$_2$(OH)$_2$(H$_2$O)$_8$]$^{4+}$Θ^{4-}.6(H$_2$O).

intermolecular N–H⋯N hydrogen bonds giving columns of cyclam held together by alternating pairs of intermolecular hydrogen bonds at N–H⋯N distances of 2.296 and 2.267 Å (corresponding N⋯N 3.155 and 3.143 Å). The intermolecular hydrogen bonds are considerably more direct than the intra-molecular hydrogen bonds with N–H⋯N angles of 178.1 and 177.0°.

In the structure of [Cr$_2$(OH)$_2$(H$_2$O)$_8$]$^{4+}$Θ^{4-}.6(H$_2$O) the [H$_4$(cyclam)]$^{4+}$ is locked within the capsule by an intricate hydrogen bonded array [Fig. 2(*a*)]. Protons were not found crystallographically and the hydrogen bonding network is implied through numerous close N⋯O contacts ranging from 2.61 to 2.83 Å. There are close N⋯O contacts, in addition to those shown in Fig. 2(*a*), with a sulfonate group of another capsule and a water molecule, hence each N-centre is associated with at least two hydrogen bonds, which, along with its *exodentate* conformation,[2] is good evidence that the cyclam is the tetra-protonated species [H$_4$(cyclam)]$^{4+}$. The capsule itself is not as symmetrical as those containing crown ether,[6] with the two bowl cavities offset relative to each other, presumably to maximise hydrogen bonding and for geometrical comple-mentarity between the interacting hydrophobic components of the cyclam and calixarene. The conformation of the calixarene, however, is more symmetrical than for the crown ether ionic capsules where two opposite phenol groups are splayed apart, with dihedral angles 93–100° relative to the other two, dihedral angle 46–59°.[6] In the present structure the corresponding dihedral angles are 81 and 52°. Packing of the capsules within the crystal lattice shows sulfonate to hydroxy hydrogen bonding between calixarenes of adjacent capsules (O⋯O separations of 2.87 and 2.90 Å) complemented by a slightly displaced π stacking of phenyl groups (centroid separation 3.62 Å, closest C⋯C = 3.43 Å, torsion angle between aromatic faces = 0°) [Fig. 2(*b*)]. The dichromium cations sit at the hydrophilic equator of the capsules [Fig. 2(*b*)], with close O⋯O contacts between the coordinated waters and sulfonate groups ranging

from 2.62 to 2.77 Å. The geometry of the dichromium cation is unexceptional[6,10] and deviates from strict octahedral coor-dination.

Overall, we have established new supramolecular chemistry of cyclam, that of pure cyclam as a reference point in the area, and that of the capsule which gives further insight into construction of ionic capsules.

Notes and references

† Synthesis of [Cr$_2$(OH)$_2$(H$_2$O)$_8$$^{4+}$Θ^{4-}: An aqueous solution of sodium *p*-sulfonatocalix[4]arene and cyclam in 2 : 1 proportions was added to an aqueous solution of [Cr$_2$(OH)$_2$(H$_2$O)$_8$][ClO$_4$]$_4$ and the pH of the mixture was adjusted to pH 2.0 with aqueous HClO$_4$. Pale green crystals of [Cr$_2$(OH)$_2$(H$_2$O)$_8$]$^{4+}$Θ^{4-} grew as a hexahydrate over several weeks. Crystals were sensitive to loss of solvent, becoming opaque on removal from mother liquor.
‡ Data were collected at 123(1) K on an Enraf-Nonius KappaCCD diffractometer with Mo-Kα radiation, λ = 0.71073 Å. Structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares on F^2 (SHELXL-97). *Crystal data* for Cyclam: C$_{10}$H$_{24}$N$_4$, M_r = 200.33, crystal size = 0.23 × 0.18 × 0.13 mm, triclinic, $P\bar{1}$, a = 4.6353(3), b = 8.5958(6), c = 15.2418(10) Å, α = 90.704(3), β = 96.743(4), γ = 99.336(4)°, V = 594.80(6) Å^3, Z = 2, μ = 0.07 mm^{-1} (no correction), $2\theta_{max}$ = 60.14°, 4366 data collected, 2989 unique (R_{int} = 0.023), 223 parameters, final GoF = 1.040, R_1 = 0.0498 [on 2198 observed data with $I > 2\sigma(I)$], wR_2 = 0.1099 (all data). All nonhydrogen atoms were refined anisotropically and all hydrogen atoms were located in the difference map and fully refined isotropically. For [Cr$_2$(OH)$_2$(H$_2$O)$_8$$^{4+}$Θ^{4-}.6(H$_2$O): C$_{33}H_{77}CrN_2O_{27}S_4$, M_r = 1114.21, crystal size = 0.18 × 0.08 × 0.04 mm, triclinic, $P\bar{1}$, a = 10.9916(3), b = 14.8774(5), c = 15.3517(6) Å, α = 63.836(1), β = 86.583(2), γ = 80.499(2)°, V = 2222.03(13) Å^3, Z = 2, μ = 0.545 mm^{-1} (no correction), $2\theta_{max}$ = 54.44°, 37347 data collected, 9727 unique (R_{int} = 0.146), 613 parameters, final GoF = 2.277, R_1 = 0.1644 [on 9727 observed data with $I > 2\sigma(I)$], wR_2 = 0.2347 (all data). All nonhydrogen atoms were refined anisotropically and C–H hydrogens were fixed at geometrically calculated positions. High residuals are a con-sequence of the extremely small, needle-like crystals obtained and poor data quality indicated by the high R_{int}. CCDC 182/1249. See http://www.rsc.org/suppdata/cc/1999/1137/ for crystallographic files in .cif format.

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