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Diazacoronand linked β-cyclodextrin† dimer complexes of Brilliant Yellow tetraanion and their sodium(I) analogues‡

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Complexation of the Brilliant Yellow tetraanion, $\mathbf{3}^{4-}$, by two new diazacoronand linked β-cyclodextrin (βCD) dimers 4,13-bis(2-(6^{A}-deoxy-β-cyclodextrin-6^{A}-yl)aminoethylamidomethyl- and 4,13-bis(8-(6^{A}-deoxy-β-cyclodextrin-6^{A}-yl)aminooctylamidomethyl)-4,13-diaza-1,7,10-trioxacyclopentadecane, **1** and **2**, respectively, has been studied in aqueous solution. UV-visible spectrophotometric studies at 298.2 K, pH 10.0 and $I = 0.10$ mol dm^{-3} (NEt_4ClO_4) yielded complexation constants for the complexes $\mathbf{1}\cdot\mathbf{3}^{4-}$ and $\mathbf{2}\cdot\mathbf{3}^{4-}$, $K_1 = (1.08 \pm 0.01) \times 10^5$ and $(6.21 \pm 0.08) \times 10^3$ dm^3 mol^{-1}, respectively. Similar studies at 298.2 K, pH 10.0 and $I = 0.10$ mol dm^{-3} ($NaClO_4$) yielded $K_3 = (4.63 \pm 0.09) \times 10^5$ and $(3.38 \pm 0.05) \times 10^4$ dm^3 mol^{-1} for the complexation of $\mathbf{3}^{4-}$ by $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{2}$ to give $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$, respectively. Potentiometric studies of the complexation of Na^+ by **1** and **2** by the diazacoronand component of the linkers to give $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{2}$ yielded $K_2 = (2.00 \pm 0.05) \times 10^2$ and $(1.8 \pm 0.05) \times 10^3$ dm^3 mol^{-1}, respectively, at 298.2 K and $I = 0.10$ mol dm^{-3} (NEt_4ClO_4). For complexation of Na^+ by $\mathbf{1}\cdot\mathbf{3}^{4-}$ and $\mathbf{2}\cdot\mathbf{3}^{4-}$ to give $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ $K_2K_3/K_1 = K_4 = 8.6 \times 10^2$ and 9.8×10^3 dm^3 mol^{-1}, respectively. The pK_as of $\mathbf{1}H_4^{4+}$ are 7.63 ± 0.01, 6.84 ± 0.02, 5.51 ± 0.04 and 4.98 ± 0.03, and those of $\mathbf{2}H_4^{4+}$ are 8.67 ± 0.02, 8.11 ± 0.02, 6.06 ± 0.02 and 5.14 ± 0.05. The larger magnitude of K_1 for **1** by comparison with K_1 for **2** is attributed to the octamethylene linkers of **2** competing with $\mathbf{3}^{4-}$ for occupancy of the annuli of the βCD entities while the competitive ability of the dimethylene linkers of **1** is less. A similar argument applies to the relative magnitudes of K_3 for $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{2}$. Increased electrostatic attraction probably accounts for $K_3 > K_1$ for $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $\mathbf{1}\cdot\mathbf{3}^{4-}$ and for $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ and $\mathbf{2}\cdot\mathbf{3}^{4-}$. The lesser magnitudes of K_2 and K_4 for $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ compared with those for $Na^+\cdot\mathbf{2}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ are attributed to the octamethylene linkers of **2** producing a more hydrophobic environment for the diazacoronand than that produced by the dimethylene linkers of **1**. ^{1}H NMR spectroscopic studies and the syntheses of **1** and **2** are described.

Introduction

β-Cyclodextrin (βCD, Fig. 1) is the basis of a wide range of hosts constructed to complex a plethora of guests.[1,2] Apart from their intrinsic interest, such complexes have the potential to be components of molecular devices.[3,4] We are interested in building a variety of such complexes to gain a better understanding of the interactions controlling their stability. To this end, we have synthesised two new diazacoronand linked β-cyclodextrin dimers, 4,13-bis(2-(6^{A}-deoxy-β-cyclodextrin-6^{A}-yl)-aminoethylamidomethyl)- and 4,13-bis(8-(6^{A}-deoxy-β-cyclodextrin-6^{A}-yl)aminooctylamidomethyl)-4,13-diaza-1,7,10-trioxacyclodecapentane, **1** and **2**, where the linker contains a metal ion binding diazacoronand (Fig. 1). Linked cyclodextrin dimers and their metal complexes are capable of binding suitably dimensioned guests in water and it is known that the length of the linker between the two βCD entities can influence the stabilities of the complexes formed.[5] Accordingly, we have chosen substantially different linker lengths in **1** and **2** to assess their effect on complexation. The Brilliant Yellow tetraanion, $\mathbf{3}^{4-}$, was chosen as the guest because its charge minimises the possibility of aggregation that characterises some extended aromatic systems,[6] it is likely to be electrostatically attracted by a metal ion bound by the diazacoronand unit and because its extended aromatic structure maximises the likelihood of complexation. In other studies CD dimers joined by metal ion binding linkers have been used as guest-selective hosts and as catalysts.[7] This study has a different emphasis in seeking to characterise all of the equilibria leading to the formation of the linked CD dimer complexes and the interactions within them.

Results and discussion

Spectrophotometric complexation studies of Brilliant Yellow tetraanion

The complexation of $\mathbf{3}^{4-}$ by βCD, **1** and **2** was studied spectrophotometrically at $[\mathbf{3}^{4-}]_{total} = 1.0 \times 10^{-5}$ mol dm^{-3} and [βCD, **1** or **2**]$_{total}$ varied in the range $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ mol dm^{-3} in 0.05 mol dm^{-3} borate buffer prepared from boric acid and either NEt_4OH or NaOH at $I = 0.10$ mol dm^{-3} adjusted with NEt_4ClO_4 and $NaClO_4$, respectively. In the latter case all of **1** and **2** are completely complexed by Na^+ in $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{2}$ as discussed below. The UV-visible absorption maximum of $\mathbf{3}^{4-}$ showed a small shift to shorter wavelengths in $\mathbf{1}\cdot\mathbf{3}^{4-}$ (523 nm) $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ (498 nm) and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ (507 nm) and no shift in $\mathbf{2}\cdot\mathbf{3}^{4-}$ (462 nm), where the wavelengths in brackets are isosbestic points consistent with $\mathbf{3}^{4-}$ existing in the free state and in one dominant complex (Figs. 2 and 3). Accordingly, the spectral variations of $\mathbf{3}^{4-}$ with changing concentrations of **1**, **2**, $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{2}$ were analysed by fitting the algorithm for the formation of a 1 : 1 complex to the experimental data at 1 nm intervals simultaneously over wavelength ranges where significant changes in absorbance occurred as described in the Experimental section and the derived complexation constants appear in Table 1 together with those for $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{2}$ derived potentiometrically as described below. The algorithms for 1 : 1 and 2 : 1, 1 : 2, and 2 : 1 complexation were also fitted to

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† β-Cyclodextrin = cyclomaltoheptaose
‡ Electronic supplementary information (ESI) available: Molar absorbance and 2D NMR ROESY spectra of **1** and **2**, and their complexes with $\mathbf{3}^{4-}$. See http://www.rsc.org/suppdata/ob/b2/b209759c/.

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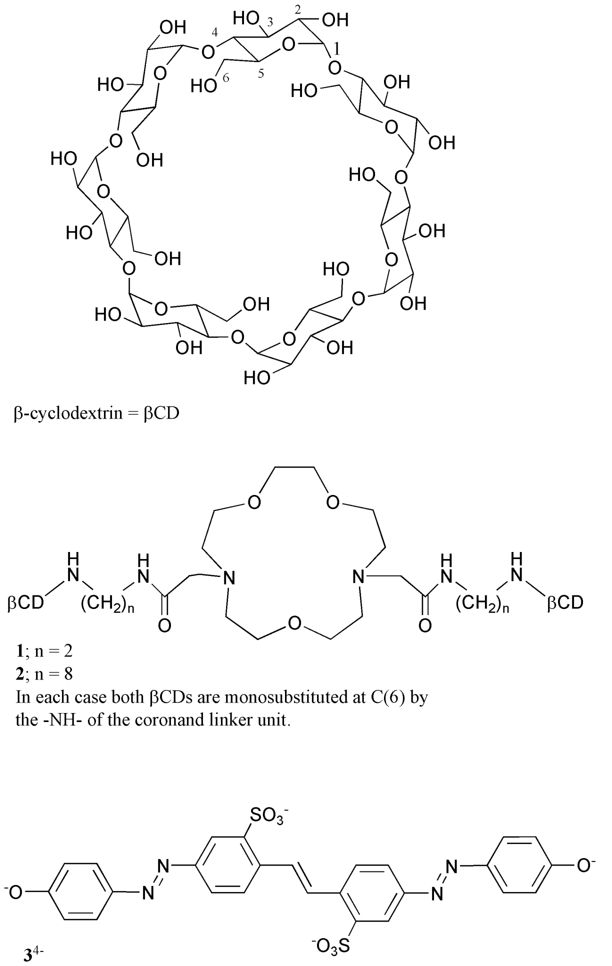
Table 1 Complexation equilibria and constants in aqueous solution at pH 10.0 (0.05 mol dm^{-3} borate buffer), $I = 0.10$ mol dm^{-3} (NEt_4ClO_4 or $NaClO_4$) and 298.2 K.

Equilibrium	Complexation constant$K$/dm^3mol^{-1} [a]
$\mathbf{1} + \mathbf{3}^{4-} \overset{K_1}{\rightleftharpoons} \mathbf{1}\cdot\mathbf{3}^{4-}$	$(1.08 \pm 0.01) \times 10^{5}$ [b]
$\mathbf{2} + \mathbf{3}^{4-} \overset{K_1}{\rightleftharpoons} \mathbf{2}\cdot\mathbf{3}^{4-}$	$(6.21 \pm 0.08) \times 10^{3}$ [b]
$Na^+ + \mathbf{1} \overset{K_2}{\rightleftharpoons} Na^+\cdot\mathbf{1}$	$(2.00 \pm 0.05) \times 10^{2}$ [b]
$Na^+ + \mathbf{2} \overset{K_2}{\rightleftharpoons} Na^+\cdot\mathbf{2}$	$(1.80 \pm 0.05) \times 10^{3}$ [b]
$Na^+\cdot\mathbf{1} + \mathbf{3}^{4-} \overset{K_3}{\rightleftharpoons} Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$	$(4.63 \pm 0.09) \times 10^{5}$ [c]
$Na^+\cdot\mathbf{2} + \mathbf{3}^{4-} \overset{K_3}{\rightleftharpoons} Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$	$(3.38 \pm 0.05) \times 10^{4}$ [c]
$Na^+ + \mathbf{1}\cdot\mathbf{3}^{4-} \overset{K_4}{\rightleftharpoons} Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$	8.6×10^{2} [d]
$Na^+ + \mathbf{2}\cdot\mathbf{3}^{4-} \overset{K_4}{\rightleftharpoons} Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$	9.8×10^{3} [d]
$\beta CD + \mathbf{3}^{4-} \overset{K}{\rightleftharpoons} \beta CD\cdot\mathbf{3}^{4-}$	$(2.2 \pm 0.05) \times 10^{3}$ [c]

[a] Errors represent one standard deviation. [b] NEt_4ClO_4 supporting electrolyte. [c] $NaClO_4$ supporting electrolyte. [d] $K_4 = K_2K_3/K_1$.



β-cyclodextrin = βCD

1; n = 2
2; n = 8
In each case both βCDs are monosubstituted at C(6) by the -NH- of the coronand linker unit.

Fig. 1 Structures of βCD and **1** and **2**.

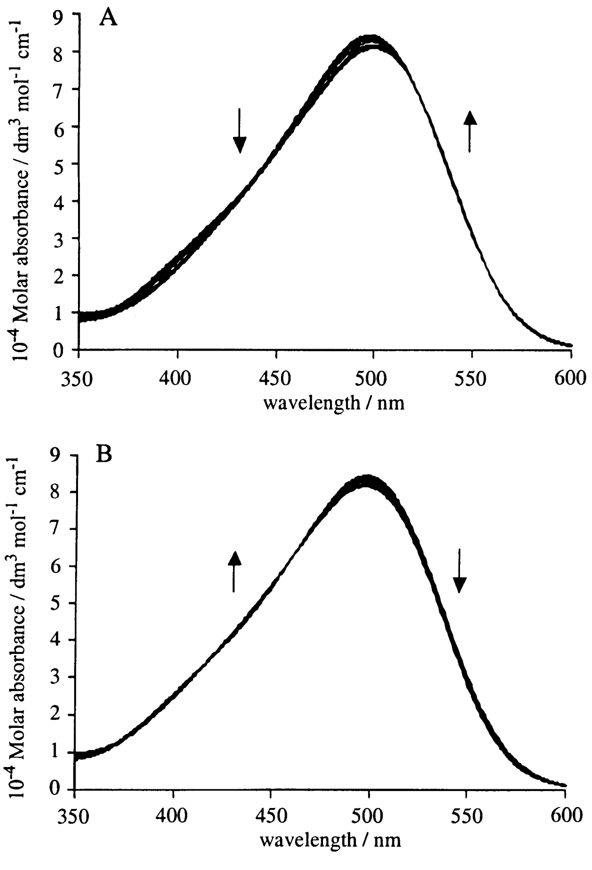


Fig. 2 Variation of the UV-visible spectrum of 1.00×10^{-5} dm^3 mol^{-1} $\mathbf{3}^{4-}$ at 298.2 K in 0.05 mol dm^{-3} aqueous $B(OH)_3/NEt_4OH$ buffer at pH 10.0 and $I = 0.10$ mol dm^{-3} (NEt_4ClO_4) in the presence of **1**, A, (523 nm) and **2**, B, (462 nm) where in each case the concentration was varied in the range 1.00×10^{-6} to 1.00×10^{-3} mol dm^{-3} and the quantities in brackets refer to isosbestic points. The absorbance changes with increasing concentration in the direction shown by the arrows.

the spectral variations but in each case the best fit was obtained with the 1 : 1 model as assessed from the magnitude of the least squares error of the fit. Two typical absorbance changes at single wavelengths are shown for the formation of $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ in Fig. 4 and $\mathbf{1}\cdot\mathbf{3}^{4-}$ and $\mathbf{2}\cdot\mathbf{3}^{4-}$ in Fig. S1. The equilibria between the complexes formed by **1** and **2** are shown schematically in Fig. 5. The spectral changes shown by $\mathbf{3}^{4-}$ on complexation are modest probably because the sulfonate

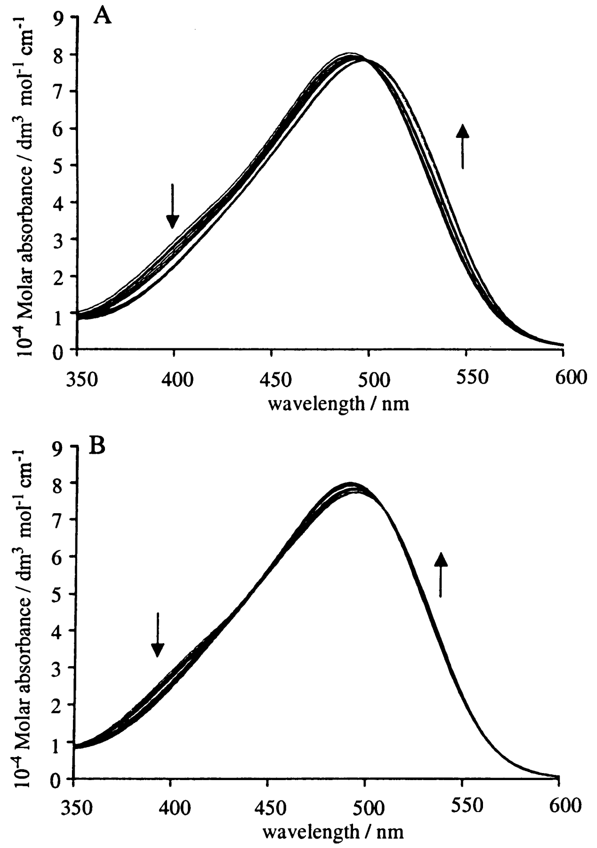


Fig. 3 Variation of the UV-visible spectrum of 1.00×10^{-5} dm^3 mol^{-1} 3^{4-} at 298.2 K in 0.05 mol dm^{-3}aqueous $B(OH)_3$/NaOH buffer at pH 10.0 and $I = 0.10$ mol dm^{-3} ($NaClO_4$) in the presence of Na^+•**1**, A, (498 nm) and Na^+•**2**, B, (507 nm) where in each case the concentration was varied in the range 1.00×10^{-6} to 1.00×10^{-3} mol dm^{-3} and the quantities in brackets refer to isosbestic points. The absorbance changes with increasing concentration in the direction shown by the arrows.

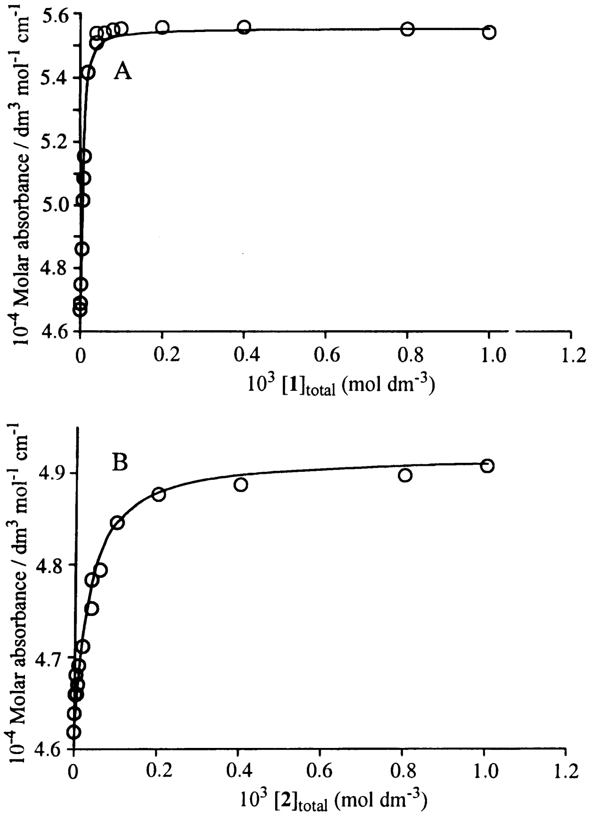


Fig. 4 A and B; variations of the molar absorbance of 1.00×10^{-5} dm^3 mol^{-1} 3^{4-} at 530 nm at 298.2 K in 0.05 mol dm^{-3} aqueous $B(OH)_3$/ NaOH buffer at pH 10.0 and $I = 0.10$ mol dm^{-3} ($NaClO_4$) with increasing concentrations of $[Na^+\cdot\mathbf{1}]_{total}$ and $[Na^+\cdot\mathbf{2}]_{total}$, respectively. The curves represent the best fit of the algorithm for the formation of $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$, respectively, to molar absorbance data at 1 nm intervals over the range 380–550 nm.

groups which are strongly hydrated in the free dye remain so in the complexed state such that the overall environmental change experienced by $\mathbf{3}^{4-}$ is also modest.

The greater stability of $\mathbf{1}\cdot\mathbf{3}^{4-}$ ($K_1 = 1.08 \times 10^5$ dm^3 mol^{-1}) by comparison with that of $\mathbf{2}\cdot\mathbf{3}^{4-}$ ($K_1 = 6.21 \times 10^3$ dm^3 mol^{-1}) is attributed to the self-complexation of the octamethylene linkers of **2** competing with $\mathbf{3}^{4-}$ for occupancy of the βCD annuli for which ^{1}H NMR evidence is presented below. As a consequence, **2** is only three times as effective in complexing $\mathbf{3}^{4-}$ as is βCD in βCD·$\mathbf{3}^{4-}$ ($K_1 = 2.20 \times 10^3$ dm^3 mol^{-1}).[6] This self-complexation also affects the relative stabilities of $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ ($K_3 = 4.63 \times 10^5$ and 3.38×10^4 dm^3 mol^{-1}, respectively) although the electrostatic attraction between the complexed Na^+ of $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{2}$ and $\mathbf{3}^{4-}$ does strengthen the complexation of $\mathbf{3}^{4-}$ in $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ several fold by comparison with that in $\mathbf{1}\cdot\mathbf{3}^{4-}$ and $\mathbf{2}\cdot\mathbf{3}^{4-}$. This is also reflected in the alternative path to $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ (for which $K_4 = 8.6 \times 10^2$ and 9.9×10^3 dm^3 mol^{-1}, respectively) in which Na^+ is bound more strongly than in $Na^+\cdot\mathbf{1}$ and $Na^+\cdot\mathbf{2}$ ($K_2 = 2.0 \times 10^2$ and 1.8×10^3 dm^3 mol^{-1}, respectively). This is attributed to the electrostatic attraction between complexed $\mathbf{3}^{4-}$ in $\mathbf{1}\cdot\mathbf{3}^{4-}$ and $\mathbf{2}\cdot\mathbf{3}^{4-}$ and Na^+ in the formation of $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$.

The spectrum of $\mathbf{3}^{4-}$ observed in 0.05 mol dm^{-3} borate buffer prepared from boric acid and NEt_4OH at $I = 0.10$ mol dm^{-3} adjusted with NEt_4ClO_4 differs from that observed in borate buffer prepared from boric and NaOH at $I = 0.10$ mol dm^{-3} adjusted with $NaClO_4$ at pH 10.0 (Fig. 6). The latter spectrum is shifted to shorter wavelengths (a change also seen on protonation of $\mathbf{3}^{4-}$) which probably reflects a stronger ion association of $\mathbf{3}^{4-}$ with Na^+ than with the much larger Et_4N^+.§

Potentiometric pK_a and metal ion complexation studies

The pK_a values and metal ion complexation constants were determined by potentiometric methods as described in the Experimental section. For $\mathbf{1}H_4^{4+}$ at 298.2 K and $I = 0.10$ mol dm^{-3} (NEt_4ClO_4) the pK_a values = 7.63 ± 0.01, 6.84 ± 0.02, 5.51 ± 0.04 and 4.98 ± 0.03 and those of $\mathbf{2}H_4^{4+}$ are 8.67 ± 0.02, 8.11 ± 0.02, 6.06 ± 0.02 and 5.14 ± 0.05. The octamethylene linker stabilises the protonated states of **2** by comparison with those of **1** possibly because they produce a more hydrophobic environment at the amine nitrogens by comparison with that induced by the dimethylene linkers of **1**.

The complexation constants for five metal ions appear in Table 2, from which it is seen that $\mathbf{1}H_2^{2+}$, $\mathbf{1}H^+$, **1**, $\mathbf{2}H_2^{2+}$, $\mathbf{2}H^+$ and **2** each complex metal ions. Of the alkali metal ions, only Na^+ formed detectable complexes while each of the alkaline earth ions formed complexes of stability varying in the general sequence $Mg^{2+} \ll Ca^{2+} > Sr^{2+} > Ba^{2+}$. These variations reflect

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§ In view of this it may be asked whether the derivation of K_4 in Table 1 and Fig. 5 from data obtained in different supporting electrolytes is valid. A measure of the effect of the separate presences of Na^+ and NEt_4^+ as the electrolyte cation is gained for the ratios $K_3/K_1 = 4.3$ and 5.4 for **1** and **2**, respectively, which reflect the specific effect of Na^+ complexation and general electrolyte effects. For the 4,13-(6^A-deoxy-β-cyclodextrin-6^A-yl)amidomethyl)-4,13-diaza-1,7,10-trioxacyclopentadecane analogue of **1** and **2** no Na^+ binding was detected by potentiometric methods consistent with $K_2 \leq 100$ dm^3 mol^{-1}. For this system $K_3/K_1 = 2.05$ which is attributed to either weak Na^+ complexation alone or in combination with a general electrolyte effect or to a general electrolyte effect alone. On this basis it appears that $K_3/K_1 = 4.3$ and 5.4 for **1** and **2** includes a modest specific effect of Na^+ binding in the formation of $Na^+\cdot\mathbf{1}\cdot\mathbf{3}^{4-}$ and $Na^+\cdot\mathbf{2}\cdot\mathbf{3}^{4-}$ and that the derived K_4 does incorporate a significant electrostatic interaction between Na^+ bound by the diazacoronand of the linker and complexed $\mathbf{3}^{4-}$.

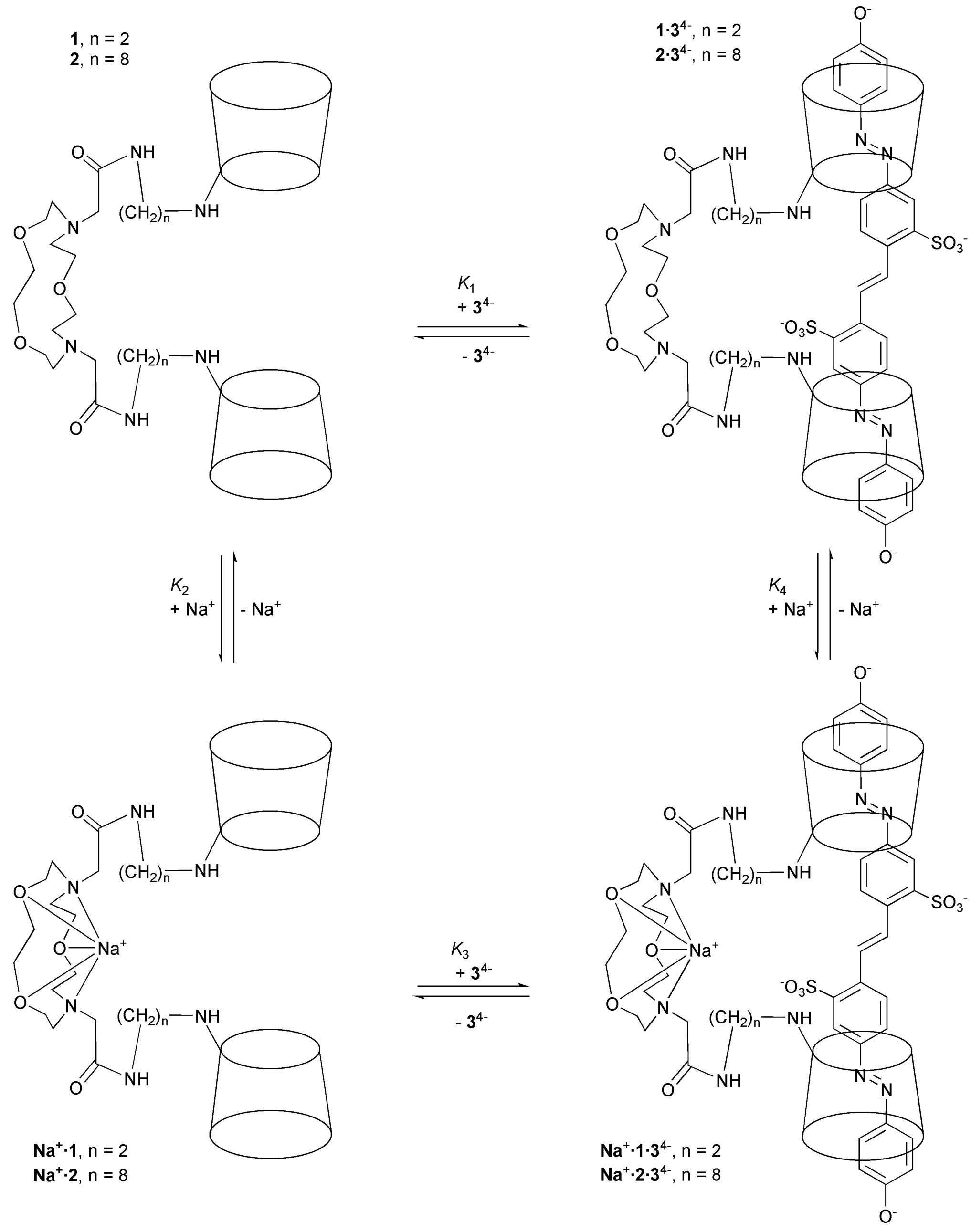

Fig. 5 Pathways for the complexation of 3^{4-} by **1** and **2**.

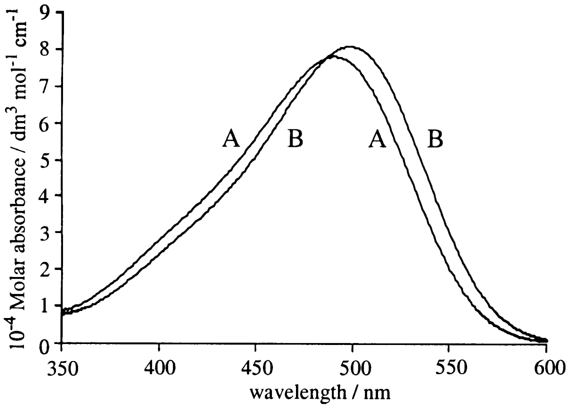

Fig. 6 UV-visible absorbance spectra of 3^{4-} (1.00×10^{-5} dm^3 mol^{-1}) at pH 10.0 in A, 0.05 mol dm^{-3} $B(OH)_3/NEt_4OH$ buffer at $I = 0.10$ mol dm^{-3} adjusted with NEt_4ClO_4 and B, 0.05 mol dm^{-3} $B(OH)_3/NaOH$ buffer at $I = 0.10$ mol dm^{-3} adjusted with $NaClO_4$ at pH 10.0.

the combined effects of metal ion hydration energies, metal ion to diazacoronand bond energies and strain energies in the complexes varying with the effective ionic radii, r_M,[8] of the metal ions. This results in five-coordinate (or six-coordinate if it assumed that six-coordination is retained through binding a water ligand) Na^+ (r_M = 100 pm and 102 pm, respectively) and Ca^{2+} (r_M = 100 pm, six-coordinate radius; no value for five-coordination is available) forming the most stable complexes in their groups. The formation of metal complexes by $\mathbf{1}H_2^{2+}$ and $\mathbf{2}H_2^{2+}$ and the increase in complex stability as deprotonation occurs is consistent with the secondary amines of the βCD substituents being the protonation sites and electrostatic repulsion between either $\mathbf{1}H_2^{2+}$, $\mathbf{1}H^+$, $\mathbf{2}H_2^{2+}$ or $\mathbf{2}H^+$ and the metal ion destabilising the complexes. The ten-fold lower stability of $Na^+\cdot\mathbf{1}$ by comparison with that of $Na^+\cdot\mathbf{2}$ is attributed to the more hydrophobic environment in the vicinity of the diazacoronand of **2** produced by the octamethylene linkers decreasing the ability of water to compete for complexation of Na^+ by comparison with the diazacoronand of **1** because of the less hydrophobic environment that it experiences in the latter case. (Under the conditions of this study no alkali or alkaline earth ion complexes were detected for 4,13-diaza-1,7,10-trioxacyclopentadecane, the precursor to **1** and **2**, consistent with $K_2 \leq$ 100 dm^3 mol^{-1} and the hydrophobic character of **1** and **2**

Table 2 Complexation constants (K) for metal complexes of **1** and **2** and their mono- and diprotonated forms at 298.2 K and I = 0.10 mol dm^{-3} (NEt_4ClO_4)[a]

	Complex and log(K/dm^{3}mol^{-1})[b]		
M^{m+}	M^{m+}·**1**H_2^{2+}	M^{m+}·**1**H^+	M^{m+}·**1**
Na^+	[c]	[c]	2.30 ± 0.05
Ca^{2+}	3.47 ± 0.07	4.59 ± 0.02	5.35 ± 0.03
Sr^{2+}	3.57 ± 0.04	4.37 ± 0.05	5.05 ± 0.02
Ba^{2+}	3.04 ± 0.04	3.81 ± 0.01	4.47 ± 0.01
M^{m+}	M^{m+}·**2**H_2^{2+}	M^{m+}·**2**H^+	M^{m+}·**2**
Na^+	2.89 ± 0.04	2.99 ± 0.05	3.26 ± 0.05
Mg^{2+}	≈2	2.53 ± 0.03	2.95 ± 0.03
Ca^{2+}	4.49 ± 0.04	4.89 ± 0.04	5.15 ± 0.03
Sr^{2+}	4.06 ± 0.05	4.45 ± 0.04	5.07 ± 0.04
Ba^{2+}	4.10 ± 0.04	4.54 ± 0.03	4.82 ± 0.03

[a] For the alkali metal ions only Na^+ complexes were detected. No complexation of Mg^{2+} by **1** or its protonated forms was detected. [b] Errors represent one standard deviation. [c] No complex detected.

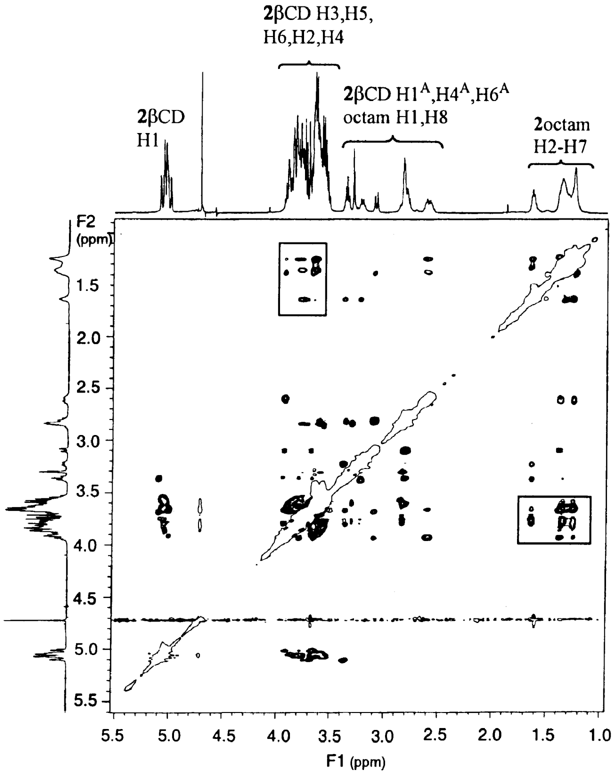

Fig. 7 The 2D ^{1}H ROESY NMR (600 MHz) spectrum of a D_2O solution 0.014 mol dm^{-3} in **2** buffered at pD 10.0 by 0.1 mol dm^{-3} ND_3/ND_4Cl buffer at 298.2 K. The rectangles enclose cross-peaks arising from ROE interactions between the H2–H7 protons of the octamethylene linkers and the βCD H3, H5 and H6 protons.

enhancing complexation. It is also possible that the two amide oxygens of **1** and **2** may interact with metal ions bound by the diazacoronand and increase complex stability. The amide oxygens of 1,7-bis(methylcarbamoylmethyl)-4,10,13-trioxa-1,7-diazacyclopentadecane[9] and 1,10-bis(*O*-methylglycylglycyl)-4,7,13,16-tetraoxa-1,10-diaza-cyclooctadecane[10] have been shown to bind Na^+ by both amide oxygens in addition to binding by the nitrogen and oxygen donor atoms of the diazacoronand ring in methanol and the solid state, respectively.) The difference in stability is much less for the more stable alkaline earth M^{2+}·**1** and M^{2+}·**2** complexes possibly because the divalent alkaline earths are more strongly hydrated. As a result dehydration energetics may be more significant compared with hydrophobic effects than is the case for the Na^+ complexes. However, the alkaline earth complexes of **1**H^+ are less stable than those of **2**H^+ and those of **1**H_2^{2+} are much less stable than those of **2**H_2^{2+}. This is consistent with the closer proximity of the protonated secondary amines of the βCD substituents in **1**H^+ and **1**H_2^{2+} generating a greater electrostatic repulsion towards alkaline earth ion complexation. At pH 10.0, solutions of the alkaline earth ions, **3**$^{4-}$ and either **1** or **2** formed precipitates which may be salts of **3**$^{4-}$. Thus, Na^+·**1** and Na^+·**2** were the only metal binding species which could be studied in the complexation of **3**$^{4-}$.

^{1}H NMR spectroscopic studies

The ^{1}H ROESY NMR (600 Mz) spectrum of **2** in D_2O is shown in Fig. 7 from which it is seen that cross-peaks arise from ROE interactions between the H2-H7 protons of the octamethylene linkers and the H3, H5 and H6 protons inside the βCD annuli consistent with self-complexation of the octamethylene linkers in the βCD annuli. (Self-complexation in linked CD dimers has been reported previously as has the self-complexation of substituents of monomeric CDs.[11]) Addition of tetraethylammonium adamantane-1-carboxylate results in the appearance of new cross-peaks arising from ROE interactions of its protons and the βCD H3, H5 and H6 protons consistent with complexation of adamantane-1-carboxylate by **2**. The intensities of these cross peaks grow and those arising from H2-H7 of the octamethylene linkers of **2** diminish as adamantane-1-carboxylate concentration is increased until a 2 : 1 mole ratio of adamantane-1-carboxylate to **2** is reached and the cross-peaks arising from the octamethylene linkers disappear consistent with adamantane-1-carboxylate competing more strongly for occupancy of the βCD annuli. (The complexation constant for the formation of βCD·adamantane-1-carboxylate = 1.8 × 10^4 dm^3 mol^{-1}.[12]) Cross peaks arising from ROE interactions between the protons of **3**$^{4-}$ and the βCD H3, H5 and H6 of Na^+·**2** are observed in the presence of 0.10 mol dm^{-3} $NaClO_4$ at pD ≈ 11 consistent with complexation in Na^+·**2** also (Fig. S2). On addition of two equivalents of sodium adamantane-1-carboxylate, these cross peaks are also replaced by those arising from ROE interactions between the adamantane-1-carboxylate protons and the βCD H3, H5 and H6. No evidence for self-complexation in either **1** or Na^+·**1** was found probably because the dimethylene linkers are too short.

The ^{1}H ROESY NMR (600 Mz) spectra of equimolar solutions of either **1** or **2** and **3**$^{4-}$ in 0.1 mol dm^{-3} ND_3/ND_4Cl buffer at pD 10.0 in D_2O are characterised by strong-cross peaks arising from ROE interactions between the protons of **3**$^{4-}$ and the βCD H3, H5 and H6 of **2** consistent with the complexation of **3**$^{4-}$ in the βCD annuli of **1** and **2** in **1**·**3**$^{4-}$ and **2**·**3**$^{4-}$, respectively (Figs. S3 and S4‡). This is also the case for equimolar solutions of either **1** or **2** and **3**$^{4-}$ in 10^{-3} mol dm^{-3} NaOD and 0.10 mol dm^{-3} in $NaClO_4$ (pD ≈ 11) consistent with the formation of Na^+·**1**·**3**$^{4-}$ and Na^+·**2**·**3**$^{4-}$ complexes (Fig. S5‡ and Fig. 8), respectively. It is seen from Fig. 8 that there are no cross-peaks arising from ROE interactions between H2–H7 of the octamethylene linkers and βCD H3, H5 and H6 consistent with the self-complexation process being weaker than the complexation of **3**$^{4-}$ in Na^+·**2**·**3**$^{4-}$. A similar situation applies in the spectrum of **2**·**3**$^{4-}$ (Fig. S4‡).

Conclusion

The linked βCD dimers, **1** and **2** and their Na^+·**1** and Na^+·**2** complexes bind **3**$^{4-}$ moderately to form **1**·**3**$^{4-}$, Na^+·**1**·**3**$^{4-}$, **2**·**3**$^{4-}$ and Na^+·**2**·**3**$^{4-}$, respectively, where the latter two complexes are less stable as a consequence of the self-complexation of the octamethylene linkers of **2** competing with **3**$^{4-}$ for occupancy of the βCD annuli. The moderately greater stabilities of Na^+·**1**·**3**$^{4-}$

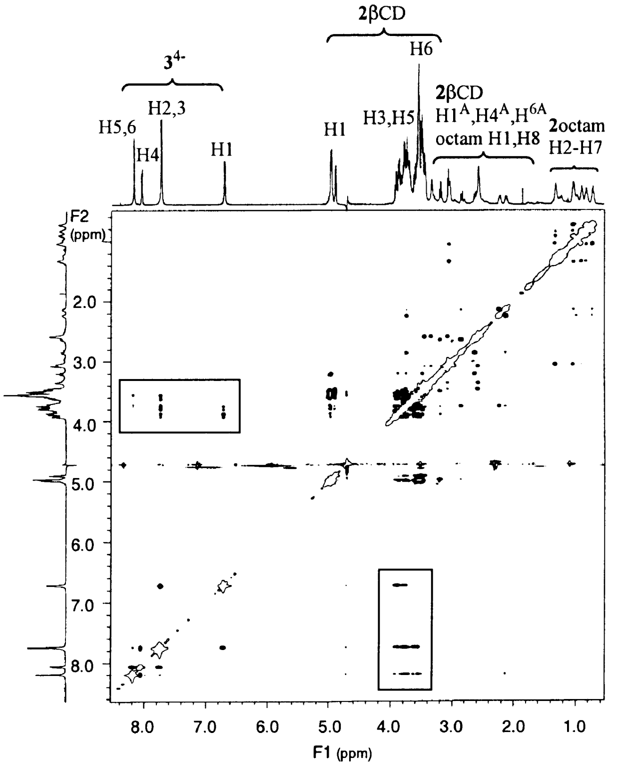

Fig. 8 The 2D ^{1}H ROESY NMR (600 MHz) spectrum of a D_2O solution 0.014 mol dm^{-3} in **2** and $\mathbf{3}^{4-}$ in 10^{-3} mol dm^{-3} NaOD and 0.1 mol dm^{-3} in $NaClO_4$ (pD ≈ 11) at 298.2 K. The rectangles enclose the cross-peaks arising from ROE interactions between the protons of $\mathbf{3}^{4-}$ and the βCD H3, H5 and H6 protons.

and $Na^+{\cdot}\mathbf{2}{\cdot}\mathbf{3}^{4-}$ by comparison with those of $\mathbf{1}{\cdot}\mathbf{3}^{4-}$ and $\mathbf{2}{\cdot}\mathbf{3}^{4-}$, respectively, are attributed to the electrostatic attraction of complexed Na^+ for $\mathbf{3}^{4-}$. Similarly, the moderately greater stabilities of $Na^+{\cdot}\mathbf{1}{\cdot}\mathbf{3}^{4-}$ and $Na^+{\cdot}\mathbf{2}{\cdot}\mathbf{3}^{4-}$ by comparison with those of $Na^+{\cdot}\mathbf{1}$ and $Na^+{\cdot}\mathbf{2}$, respectively, are attributed to the electrostatic attraction of complexed $\mathbf{3}^{4-}$ for Na^+. Thus, the hydrophobic driving force underlying the complexation of $\mathbf{3}^{4-}$ in the βCD annuli of **1** and **2** has superimposed upon it self-complexation processes and electrostatic attraction forces which combine to determine the stabilities of the eight complexes formed.

Experimental

General

Aqueous solutions were prepared with water purified with a Waters Milli-Q system to give a specific resistance of >15 MΩ cm which was then boiled for 30 min to remove CO_2 and allowed to cool in a container fitted with a soda lime guard tube. Metal perchlorates (Fluka) were twice recrystallised from water, and the anhydrous salts were was obtained by drying to constant weight over P_2O_5 under vacuum prior to use. (**CAUTION**. Anhydrous perchlorate salts are potentially explosive and should be handled with care.) The disodium salt of Brilliant Yellow (Aldrich 70%) was twice recrystallised from methanol. The tetrahydrated di-tetraethylammonium salt of Brilliant Yellow was prepared as previously described.[6] UV-visible spectra of $\mathbf{3}^{4-}$ alone or in the presence of either **1** or **2** in 0.05 mol dm^{-3} borate buffer (total buffer concentration at pH 10.0 prepared from boric acid and either NEt_4OH or NaOH at I = 0.10 mol dm^{-3} adjusted with NEt_4ClO_4 and $NaClO_4$, respectively) were run at 298.2 ± 0.1 K in matched quartz cuvettes of 1 cm path length against a reference containing the same buffer and supporting electrolyte. Absorbance data were collected at 1 nm intervals with a Cary 300 Bio double beam spectrophotometer. Wavelength ranges where the greatest absorbance change occurred were selected for analysis. These ranges were 470–520 nm for $\mathbf{1}/\mathbf{3}^{4-}$, 480–550 for $\mathbf{2}/\mathbf{3}^{4-}$, 380–550 nm for $Na^+/\mathbf{1}/\mathbf{3}^{4-}$ and for 380–550 nm $Na^+/\mathbf{2}/\mathbf{3}^{4-}$.

Complex stoichiometry and complexation constants were determined through non-linear least squares fitting of algorithms for the formation of 1 : 1, 1 : 1 and 2 : 1, 1 : 2, and 2 : 1 complexes to the absorbance variation of $\mathbf{3}^{4-}$ with concentration of **1** and **2** at 1 nm intervals by using Method 5 of Pitha and Jones,[13] through an in-house least squares regression routine DATAFIT[14] using the MATLAB formalism.[15] Taking the $\mathbf{1}/\mathbf{3}^{4-}$ system as an example, the observed absorbance, A, is related to the molar absorbances of the species in solution, ε, and their concentrations through:

$$A = \varepsilon_1[\mathbf{1}] + \varepsilon_3[\mathbf{3}^{4-}] + \varepsilon_{1\cdot 3}[\mathbf{1}{\cdot}\mathbf{3}^{4-}]$$

where $\varepsilon_1 = 0$ and species concentrations are related through the complexation constant $K_2 = [\mathbf{1}{\cdot}\mathbf{3}^{4-}]/([\mathbf{1}][\mathbf{3}^{4-}])$.

^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were run on a Varian Gemini 300 spectrometer, and ^{1}H (600 MHz) NMR spectra were run on an Inova 600 spectrometer. Solutions of $\mathbf{3}^{4-}$ alone or in the presence of either **1** or **2** were prepared to give concentrations of 0.013–0.015 mol dm^{-3} in each constituent in either 0.10 mol dm^{-3} ND_3/ND_4Cl buffer at pD 10.0 or 10^{-3} mol dm^{-3} NaOD and 0.1 mol dm^{-3} in $NaClO_4$ (pD ≈ 11) in D_2O. Chemical shifts were referenced against external trimethylsilylpropiosulfonic acid. ESI mass spectrometric studies were made in positive ion mode with a Finnigan MAT ion trap LC–Q mass spectrometer fitted with an electrospray ionisation source. Accurate mass spectrometry was carried out at the University of Tasmania, Hobart. Samples were dissolved in water for injection. Elemental analyses were performed by the Microanalytical Service of the Chemistry Department, University of Otago, Dunedin, New Zealand. Both **1** and **2** decomposed upon heating which precluded the determination of melting points. All reagents used were obtained from Aldrich and were not further purified before use, unless otherwise stated. βCD (Nihon Shokuhuin Kako Co.) was dried by heating at 100 °C under vacuum for 18 h. All solvents used in syntheses were redistilled and dried by standard methods.

Potentiometric titrations were carried out using a Metrohm Dosimat E665 titrimeter, an Orion SA 720 potentiometer and an Orion 8172 Ross Sureflow combination pH electrode that was filled with 0.10 mol dm^{-3} either NEt_4ClO_4 or $NaClO_4$. Titration solutions were saturated with nitrogen by passing a fine stream of bubbles (previously passed through aqueous 0.10 mol dm^{-3} NaOH followed by 0.10 mol dm^{-3} $NaClO_4$) through them for at least 15 min before the commencement of the titration. During the titrations a similar stream of nitrogen bubbles was passed through the titration solution which was magnetically stirred and held at 298.2 ± 0.1 K in a water-jacketed 20 cm^3 titration vessel which was closed to the atmosphere except for a small vent for nitrogen. Either standardised 0.10 mol dm^{-3} NEt_4OH or NaOH was titrated against solutions that were 1.0×10^{-3} mol dm^{-3} in the species of interest, 5.0×10^{-3} mol dm^{-3} in $HClO_4$ and 9.5×10^{-2} mol dm^{-3} in either NEt_4ClO_4 or NaClO4 (I = 0.10 mol dm^{-3}). Values of E_0 and pK_w were determined by titration of a solution that was 1.00×10^{-4} mol dm^{-3} in $HClO_4$ and 9.0×10^{-4} mol dm^{-3} in $NaClO_4$ against 0.100 mol dm^{-3} NaOH. Values of pK_a were determined using the program SUPERQUAD.[16] At least three runs were performed for each system and at least two of these runs were averaged; the criterion for selection for this averaging being that χ^2 for each run was < 12.6 at the 95% confidence level.

Syntheses

6^A-*O*-(4-methylbenzenesulfonyl)-β-cyclodextrin,[17] 4,13-bis(carboxymethyl)-4,13-diaza-1,7,10-trioxacyclopentadecane[18] and

6^{A}-(2-aminoethyl)amino-6^{A}-deoxy-β-cyclodextrin[19] were prepared by literature methods and good elemental analyses and ^{1}H and ^{13}C NMR spectroscopic data were obtained. Other reagents (Aldrich) were used as received.

6^{A}-(8-Aminooctyl)amino)-6^{A}-deoxy-β-cyclodextrin. A solution of 6^{A}-*O*-(4-methylbenzenesulfonyl)-β-cyclodextrin (2.028 g, 1.57×10^{-3} mol) and 1,8-diaminooctane (0.68 g, 4.72×10^{-3} mol) in 1-methylpyrrolidin-2-one (5 cm^3) was stirred at 70 °C for 18 h. The cooled reaction mixture was diluted with ethanol (100 cm^3) and the resultant precipitate was collected by vacuum filtration and washed with ethanol (50 cm^3) and ether (50 cm^3). The solid was dissolved in water (10 cm^3) and loaded onto a column of BioRex 70 cation exchange resin (H^+ form, 4.5 × 4.5 cm). The column was washed with water (200 cm^3) and the product was eluted with 1 mol dm^{-3} ammonia solution. Fractions containing the product were combined and evaporated under reduced pressure. The residue was dissolved in water and the solution was filtered (0.02 μm) and freeze-dried to give 6^{A}-(8-aminooctyl)amino-6^{A}-deoxy-β-cyclodextrin as a white powder (1.117 g, 56%). δ_H (300 MHz, D_2O, pD ≈ 11) 4.88 (br s, 7H, H1), 3.5–3.9 (m, 26H, H3, H5, $H6^{B–G}$), 3.3–3.5 (m, 13H, H2, H4), 3.12 (t, $J = 9.0$ Hz, 1H, $H4^{A}$), 2.87 (br d, $J = 12.0$ Hz, 1H, $H6^{A}$), 2.6 (m, 3H, $H6^{A'}$, octamethylene H1), 2.4 (m, 2H, octamethylene H8), 1.0–1.5 (m, 12H, octamethylene H2–7); δ_C (75.4 MHz, D_2O, pD ≈ 11) 109.0, 108.8, 108.5, 107.7 (C1), 90.3 ($C4^{A}$), 87.6, 87.4, 87.3, 86.5 (C4), 80.3, 80.0, 79.9, 79.6, 79.0, 78.5, 78.2, 78.1 (C2, C3, C5), 74.3 ($C5^{A}$), 66.3 (C6), 53.9 (octamethylene C8), 52.3 ($C6^{A}$), 46.9 (octamethylene C1), 38.2, 34.0, 33.2, 32.2, 31.9 (octamethylene C2–7). ESI-ms *m*/*z* 1262 ($M+H^+$). Elemental analysis for **6**·$2H_2O$ ($C_{50}H_{92}N_2O_{36}$) C, 46.29, H, 7.14, N, 2.16. Found: C, 46.31, H, 6.92, N, 2.22.

4,13-Bis(2-(6^{A}-deoxy-β-cyclodextrin-6^{A}-yl)aminoethylamidomethyl)-4,13-diaza-1,7,10-trioxacyclopentadecane, 1. A mixture of 4,13-bis(carboxymethyl)-4,13-diaza-1,7,10-trioxacyclopentadecane (0.107 g, 0.244×10^{-3} mol), 4-nitrophenol (0.070 g, 0.504×10^{-3} mol) and dicyclohexylcarbodiimide (0.108 g, 0.524×10^{-3} mol) in dichloromethane (5 cm^3) was stirred at room temperature for 2 h. The reaction mixture was filtered through Celite and the filtrate was evaporated under reduced pressure to give the crude bis(4-nitrophenyl)ester as a yellow oil (I.R. 1763 cm^{-1}). The oil was dissolved in *N*,*N*-dimethylformamide (5 cm^3) and 6^{A}-(2-aminoethyl)amino-6^{A}-deoxy-β-cyclodextrin (0.578 g, 0.491×10^{-3} mol) was added. The resultant yellow solution was stirred at room temperature for 18 h and then diluted with ether (50 cm^3). The precipitated product was collected by vacuum filtration and dissolved in water (20 cm^3). The solution was passed down a column of AG 4X4 anion exchange resin (free base form, 4.5 × 4.5 cm) which was eluted with water (100 cm^3). The eluent was concentrated under reduced pressure to 10 cm^3 and loaded onto a column of BioRex 70 cation exchange resin (NH_4^+ form, 4.5 × 4.5 cm) which was eluted sequentially with water (100 cm^3) and 0.05 mol dm^{-3} ammonium hydrogen carbonate, taking 20 cm^3 fractions. Fractions containing the product were combined and evaporated under reduced pressure. The residue was dried over P_2O_5 at room temperature under vacuum to give the product as a white powder (0.346 g, 53%). δ_H (300 MHz, D_2O, pD ≈ 11) 4.9 (bs, 14H, H1), 3.0–4.0 (m, 102H, βCD–H, diazacoronand-H), 2.6–2.8 (m, 14H, $H6^{A'}$, dimethylene H1, NC**H**$_2$). δ_C (75.4 MHz, D_2O, pD ≈ 11) 176.5, 173.6 (CO), 105.3 (C1), 86.9 ($C4^{A}$), 84.2 (C4), 76.3, 75.5, 74.5, 72.9, 71.4, 70.1, 69.8 (C2, C3, C5, diazacoronand C–O), 63.0 (C6), 60.8, 57.3, 56.9, 51.8, 50.0, 41.0, 39.2 ($C6^{A}$, dimethylene C, diazacoronand C–N). ESI-ms *m*/*z* 2654 (M + H^+). Elemental analysis for **1**·$7H_2O$ ($C_{102}H_{188}N_6O_{80}$): C, 44.09, H, 6.82, N, 3.02. Found: C, 44.09, H, 6.95 N, 3.45.

4,13-Bis(8-(6^{A}-deoxy-β-cyclodextrin-6^{A}-yl)aminooctylamidomethyl)-4,13-diaza-1,7,10-trioxacyclopentadecane, 2. A mixture of 4,13-bis(carboxymethyl)-4,13-diaza-1,7,10-trioxacyclopentadecane (0.101 g, 0.23×10^{-3} mol), 4-nitrophenol (0.064 g, 0.46×10^{-3} mol) and dicyclohexylcarbodiimide (0.098 g, 0.48×10^{-3} mol) in dichloromethane (4 cm^3) was stirred at room temperature for 2 h. The reaction mixture was filtered through Celite and the filtrate was evaporated under reduced pressure to give the crude bis(4-nitrophenyl)ester as a yellow oil (IR 1763 cm^{-1}). The residue was dissolved in *N*,*N*-dimethylformamide (5 cm^3) and 6^{A}-(8-aminooctyl)amino)-6^{A}-deoxy-β-cyclodextrin (0.590 g, 0.46×10^{-3} mol) was added. The resultant yellow solution was stirred at room temperature for 18 h and then diluted with ether (50 cm^3). The precipitated crude linked βCD dimer was collected by vacuum filtration and dissolved in water (15 cm^3) and dilute HCl (1 cm^3). The colourless solution was washed with dichloromethane (5 × 15 cm^3) and then concentrated to 10 cm^3 under reduced pressure. The residue was diluted with ethanol (100 cm^3) and the resultant precipitate was collected by vacuum filtration. The collected solid was dissolved in water (10 cm^3) and loaded onto a column of BioRex 70 cation exchange resin (NH_4^+ form, 4.5 × 4.5 cm) which was eluted sequentially with water (100 cm^3) and 0.05 mol dm^{-3} ammonium hydrogen carbonate, taking 20 cm^3 fractions. Fractions containing the product were combined and evaporated under reduced pressure. The residue was dried over P_2O_5 at room temperature under vacuum to give the product as a white powder (0.242 g, 37%). δ_H (600 MHz, D_2O, pD ≈ 11) 4.88 (m, 14H, H1), 2.9–3.9 (m, 102H, CD–H, diazacoronand–H), 2.2–2.8 (m, 14H, $H6^{A'}$, octamethylene H1, diazacoronand C**H**$_2$-N), 1.0–1.6 (m, 24H, octamethylene H); δ_c (75.4 MHz, D_2O, pD ≈ 11) 176.3, 176.2, 176.1, 175.4 (C=O), 105.7, 105.3, 103.8 (C1), 87.4 ($C4^{A}$), 84.6, 84.5, 84.3, 84.1, 82.9 (C4), 77.5, 76.7, 75.9, 75.5, 74.8, 74.6 (C2,C3,C5), 71.5, 70.1, 69.9, 69.3 ($C5^{A}$, diazacoronand–C), 63.1, 62.7, 60.6, 57.3, 51.7, 46.4, 42.2 (C6, diazacoronand **C**–N, octamethylene C1, octamethylene C8), 31.9, 31.7, 31.5, 31.1, 30.4, 29.9, 29.7, 29.2, 29.1, 28.7, 28.4, 27.8 (octamethylene C2–7). ESI-ms *m*/*z* 2822 (M + H^+), 1412 (M + $2H^+$), 942 (M + $3H^+$). Elemental analysis for **2**·$13H_2O$ ($C_{114}H_{224}N_6O_{86}$) C, 44.82; H, 7.39; N, 2.75. Found C, 44.75; H, 6.98; N, 2.82.

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