

# Adducts of 1,4,8,11-tetraazacyclotetradecane with carboxylic acids: hydrogen-bonded supramolecular structures in two or three dimensions

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Four solvated salt-type adducts derived from cyclam (1,4,8,11-tetraazacyclotetradecane) and carboxylic acids have been structurally characterized. In the salt derived from adamantane-1-carboxylic acid, 4,11-diaza-1,8-diazoniacyclotetradecane bis(adamantane-1-carboxylate) tetrahydrate, (1) (monoclinic,  $P2_1/c$ ,  $Z' = 0.5$ ), where the cation lies across a centre of inversion, the anions and the water molecules form chains of edge-fused  $R_4^2(8)$  and  $R_6^0(16)$  rings, which are linked into sheets by the cations. In the 4-aminobenzoate salt, 4,11-diaza-1,8-diazoniacyclotetradecane bis(4-aminobenzoate) monohydrate, (2) (monoclinic,  $C2/c$ ,  $Z' = 0.5$ ), where the cation lies across a centre of inversion and the water molecule lies across a twofold rotation axis, the cations and anions generate a three-dimensional framework, readily analysed in terms of two distinct two-dimensional substructures, *viz.* (10 $\bar{1}$ ) sheets of  $R_6^0(46)$  rings, and pairwise interwoven (100) sheets, reinforced by water molecules. The 3-hydroxybenzoate salt, 4,11-diaza-1,8-diazoniacyclotetradecane bis(3-hydroxybenzoate) dihydrate, (3) (monoclinic,  $Pc$ ,  $Z' = 1$ ), contains a three-dimensional framework constructed from anions and water molecules only, which encapsulates large voids and within which the cations are linked to the anion–water framework *via* N–H $\cdots$ O hydrogen bonds. There are two independent cations in 4,11-diaza-1,8-diazoniacyclotetradecane 5-hydroxyisophthalate(2 $-$ ) methanol solvate, (4) (monoclinic,  $P2_1/c$ ,  $Z' = 1$ ), both lying across centres of inversion but with entirely different configurations. The anions alone form simple chains, and these chains are linked by the two types of cation into a three-dimensional framework from which the methanol molecules are pendent. Comparisons are made with carboxylate complexes of the  $[\text{Ni}(\text{cyclam})]^{2+}$  cation and with carboxylate salts derived from *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

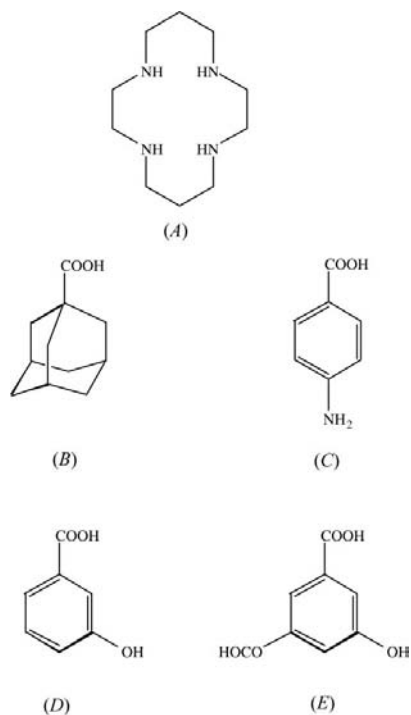
## 1. Introduction

We have recently reported (Glidewell *et al.*, 2000; Zakaria *et al.*, 2001, 2002) on the supramolecular aggregation patterns of an extensive series of complexes,  $[\text{Ni}(\text{cyclam})(\text{OCOR})_2]$  [cyclam is 1,4,8,11-tetraazacyclotetradecane,  $\text{C}_{10}\text{H}_{24}\text{N}_4$ , (A); see scheme]. Amongst the examples studied were those in which the paired anionic  $\text{RCOO}^-$  ligands, were 2-naphthoate ( $\text{C}_{10}\text{H}_7\text{COO}^-$ ), 3-hydroxybenzoate ( $\text{HOC}_6\text{H}_4\text{COO}^-$ ) and 4-aminobenzoate ( $\text{H}_2\text{NC}_6\text{H}_4\text{COO}^-$ ), together with an aquated complex,  $[\text{Ni}(\text{cyclam})\{\text{HOC}_6\text{H}_3(\text{COO})_2(\text{H}_2\text{O})\}] \cdot 4\text{H}_2\text{O}$ , containing the 5-hydroxyisophthalate(2 $-$ ) ligand (Zakaria *et al.*, 2002).

The structure of the 2-naphthoate complex,  $[\text{Ni}(\text{cyclam})(\text{OCOC}_{10}\text{H}_7)_2]$ , contains isolated molecules with neither C–

H···O nor C—H··· $\pi$ (arene) hydrogen bonds linking the complexes; nor are there any aromatic  $\pi$ – $\pi$  stacking interactions present. In the 3-hydroxybenzoate complex, [Ni(cyclam)(OCOC<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>], there is a single O—H···O hydrogen bond, which links the complexes into sheets built from  $R_4^4(36)$  rings, while in the 4-aminobenzoate complex, [Ni(cyclam)(OCOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>], two independent N—H···O hydrogen bonds link the complexes into a three-dimensional framework. The 5-hydroxyisophthalate complex likewise forms a three-dimensional hydrogen-bonded framework structure, but this is of some complexity, largely as a consequence of the heavy hydration.

We have now investigated an analogous series of systems, namely the salts formed by the interaction of cyclam itself and a comparable range of acids, in order to compare the products formed by the [Ni(cyclam)]<sup>2+</sup> unit with those formed by the metal-free cyclam. We can also compare the products derived from cyclam with those derived from its hexa-C-methyl analogue, *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-a, C<sub>16</sub>H<sub>36</sub>N<sub>4</sub>; Burchell *et al.*, 2000; Gregson *et al.*, 2000). The acids used in the present study were adamantane-1-carboxylic acid, C<sub>10</sub>H<sub>15</sub>COOH, (*B*); 4-aminobenzoic acid, H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COOH, (*C*); 3-hydroxybenzoic acid, HOC<sub>6</sub>H<sub>4</sub>COOH, (*D*); and 5-hydroxyisophthalic acid, HOC<sub>6</sub>H<sub>3</sub>(COOH)<sub>2</sub>, (*E*) (see scheme). We have employed adamantane-1-carboxylic acid in place of 2-naphthoic acid specifically to preclude any form of direction-specific interaction involving the hydrocarbyl component of the acid moiety.



The products described here are all salts containing the doubly protonated cyclam unit, [(cyclam)H<sub>2</sub>]<sup>2+</sup>, namely

4,11-diaza-1,8-diazoniacyclotetradecane bis(adamantane-1-carboxylate) tetrahydrate, C<sub>10</sub>H<sub>26</sub>N<sub>4</sub>·2C<sub>11</sub>H<sub>15</sub>O<sub>2</sub>·4H<sub>2</sub>O, (1); 4,11-diaza-1,8-diazoniacyclotetradecane bis(4-aminobenzoate) monohydrate, C<sub>10</sub>H<sub>26</sub>N<sub>4</sub>·2C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub>·H<sub>2</sub>O, (2); 4,11-diaza-1,8-diazoniacyclotetradecane bis(3-hydroxybenzoate) dihydrate, C<sub>10</sub>H<sub>26</sub>N<sub>4</sub>·2C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>·2H<sub>2</sub>O, (3); and 4,11-diaza-1,8-diazoniacyclotetradecane 5-hydroxyisophthalate(2–) methanol solvate, C<sub>10</sub>H<sub>26</sub>N<sub>4</sub>·C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>·CH<sub>4</sub>O, (4).

## 2. Experimental

### 2.1. Syntheses

Stoichiometric quantities of cyclam and the appropriate carboxylic acid, based on an intended ratio of two carboxyl groups per cyclam unit, were separately dissolved in methanol. The solutions were mixed and the mixtures were then set aside to crystallize, providing samples of compounds (1)–(4). Analyses found for (1): C 61.2, H 10.4, N 8.8%; C<sub>32</sub>H<sub>64</sub>N<sub>4</sub>O<sub>8</sub> requires: C 60.7, H 10.2, N 8.9%; found for (2): C 58.3, H 8.0, N 17.4%; C<sub>24</sub>H<sub>40</sub>N<sub>6</sub>O<sub>5</sub> requires: C 58.5, H 8.2, N 17.1%; found for (3): C 56.2, H 7.8, N 11.0%; C<sub>24</sub>H<sub>36</sub>N<sub>4</sub>O<sub>8</sub> requires: C 56.2, H 7.9, N 10.9%; found for (4): C 55.0, H 8.3, N 13.3%; C<sub>19</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub> requires: C 55.1, H 8.3, N 13.5%. Single crystals suitable for X-ray diffraction were selected directly from the prepared samples.

### 2.2. Data collection, structure solution and refinement

Diffraction data for (1)–(4) were collected at 150 (2) K using a Nonius KappaCCD diffractometer and graphite-monochromated Mo *K* $\alpha$  radiation ( $\lambda = 0.71073$  Å). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed.

For (1) and (4), the space group  $P2_1/c$  was in each case assigned uniquely from the systematic absences. For (2), the systematic absences permitted  $C2/c$  and  $Cc$  as possible space groups;  $C2/c$  was selected and confirmed by the successful structure analysis. For (3), the systematic absences permitted  $P2_1/c$  and  $Pc$ , and here  $Pc$  was selected and confirmed by the analysis. The structures were all solved by direct methods and refined with all data on  $F^2$ . A weighting scheme based on  $P = [F_o^2 + 2F_c^2]/3$  was employed in order to reduce statistical bias (Wilson, 1976). In each of (1) and (2), a single cation lies across a centre of inversion, while in (4), there are two independent cations, both lying across centres of inversion. The water molecule in (2) lies on a twofold axis. The other components in these compounds all lie in general positions. All H atoms were located from difference maps and all were fully ordered. The water H atoms in (1) were placed at positions determined from the difference maps, giving O—H distances of 0.95 Å at atom O3 and 0.87 Å at atom O4; all other H atoms were included in the refinements as riding atoms, with O—H distances of 0.84 (aromatic hydroxyl) or 0.95 Å (water), N—H distances of 0.88 [in the anion of (2)] or 0.92 Å (in the cations), and C—H distances of 0.95 (aromatic), 0.98 (CH<sub>3</sub>), 0.99 (CH<sub>2</sub>) or 1.00 Å (aliphatic CH). In the

**Table 1**  
Experimental details.

|   | (1)   | (2)  | (3)   | (4)  |
|---|---|--|---|--|
| <b>Crystal data</b>                                       |   |  |   |  |
| Chemical formula  | $C_{10}H_{26}N_4 \cdot 2C_{11}H_{15}O_2 \cdot 4H_2O$  | $C_{10}H_{26}N_4 \cdot 2C_7H_6NO_2 \cdot H_2O$   | $C_{10}H_{26}N_4 \cdot 2C_7H_5O_3 \cdot 2H_2O$  | $C_{10}H_{26}N_4 \cdot C_8H_4O_5 \cdot CH_4O$  |
| $M_r$   | 632.87  | 492.62   | 512.60  | 414.50   |
| Cell setting, space group                                 | Monoclinic, $P2_1/n$  | Monoclinic, $C2/c$   | Monoclinic, $Pc$  | Monoclinic, $P2_1/c$   |
| $a, b, c$ (Å)   | 8.8604 (2), 6.80250 (10), 27.8239 (6)   | 19.6462 (8), 9.0374 (4), 15.2051 (7)   | 9.1490 (2), 12.8557 (4), 12.4022 (4)  | 9.7666 (3), 13.9931 (6), 15.9476 (6)   |
| $\beta$ (°)   | 91.0440 (10)  | 94.127 (2)   | 113.8540 (19)   | 102.280 (2)  |
| $V$ (Å <sup>3</sup> )                                     | 1676.75 (6)   | 2692.7 (2)   | 1334.10 (7)   | 2129.61 (14)   |
| $Z$   | 2   | 4  | 2   | 4  |
| $D_x$ (Mg m <sup>-3</sup> )                               | 1.254   | 1.215  | 1.276   | 1.293  |
| Radiation type  | Mo $K\alpha$  | Mo $K\alpha$   | Mo $K\alpha$  | Mo $K\alpha$   |
| No. of reflections for cell parameters                    | 3796  | 3016   | 3059  | 4886   |
| $\theta$ range (°)  | 2.9–27.5  | 2.7–27.3   | 2.9–27.7  | 2.7–27.6   |
| $\mu$ (mm <sup>-1</sup> )                                 | 0.09  | 0.09   | 0.10  | 0.10   |
| Temperature (K)   | 150 (2)   | 150 (2)  | 150 (2)   | 150 (2)  |
| Crystal form, colour                                      | Block, colourless   | Plate, colourless  | Block, colourless   | Block, colourless  |
| Crystal size (mm)   | 0.35 × 0.25 × 0.22  | 0.32 × 0.29 × 0.14   | 0.30 × 0.28 × 0.22  | 0.20 × 0.16 × 0.16   |
| <b>Data collection</b>                                    |   |  |   |  |
| Diffractometer  | Nonius KappaCCD   | Nonius KappaCCD  | Nonius KappaCCD   | Nonius KappaCCD  |
| Data collection method                                    | $\varphi$ scans, and $\omega$ scans with $\kappa$ offsets   | $\varphi$ scans, and $\omega$ scans with $\kappa$ offsets  | $\varphi$ scans, and $\omega$ scans with $\kappa$ offsets   | $\varphi$ scans, and $\omega$ scans with $\kappa$ offsets  |
| No. of measured, independent and observed parameters      | 10461, 3796, 2910   | 12532, 3016, 2156  | 9540, 3059, 2693  | 16817, 4886, 3059  |
| Criterion for observed reflections                        | $I > 2\sigma(I)$  | $I > 2\sigma(I)$   | $I > 2\sigma(I)$  | $I > 2\sigma(I)$   |
| $R_{int}$   | 0.035   | 0.046  | 0.039   | 0.075  |
| $\theta_{max}$ (°)  | 27.5  | 27.3   | 27.7  | 27.6   |
| Range of $h, k, l$  | 0 $\Rightarrow$ $h \Rightarrow$ 11<br>0 $\Rightarrow$ $k \Rightarrow$ 8<br>-36 $\Rightarrow$ $l \Rightarrow$ 36 | 0 $\Rightarrow$ $h \Rightarrow$ 25<br>0 $\Rightarrow$ $k \Rightarrow$ 11<br>-19 $\Rightarrow$ $l \Rightarrow$ 19 | 0 $\Rightarrow$ $h \Rightarrow$ 11<br>-16 $\Rightarrow$ $k \Rightarrow$ 0<br>-16 $\Rightarrow$ $l \Rightarrow$ 14 | 0 $\Rightarrow$ $h \Rightarrow$ 12<br>0 $\Rightarrow$ $k \Rightarrow$ 18<br>-20 $\Rightarrow$ $l \Rightarrow$ 20 |
| <b>Refinement</b>   |   |  |   |  |
| Refinement on   | $F^2$   | $F^2$  | $F^2$   | $F^2$  |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$                       | 0.045, 0.124, 1.04  | 0.047, 0.117, 1.07   | 0.037, 0.105, 0.96  | 0.061, 0.193, 1.05   |
| No. of reflections  | 3796  | 3016   | 3059  | 4886   |
| No. of parameters   | 199   | 160  | 337   | 266  |
| H-atom treatment  | Constrained to parent site  | Constrained to parent site   | Constrained to parent site  | Constrained to parent site   |
| Weighting scheme  | $w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.6247P]$ where $P = (F_o^2 + 2F_c^2)/3$                                | $w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.3517P]$ where $P = (F_o^2 + 2F_c^2)/3$                                 | $w = 1/[\sigma^2(F_o^2) + (0.0769P)^2 + 0.064P]$ where $P = (F_o^2 + 2F_c^2)/3$                                   | $w = 1/[\sigma^2(F_o^2) + (0.1053P)^2 + 0.1884P]$ where $P = (F_o^2 + 2F_c^2)/3$                                 |
| $(\Delta/\sigma)_{max}$                                   | <0.0001   | <0.0001  | 0.006   | <0.0001  |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> ) | 0.28, -0.22   | 0.20, -0.19  | 0.28, -0.21   | 0.47, -0.32  |
| Extinction method   | None  | SHELXL97   | None  | SHELXL97   |
| Extinction coefficient                                    |   | 0.0053 (11)  |   | 0.026 (4)  |

Computer programs used: *KappaCCD Server Software* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 1997), *SHELXL97* (Sheldrick, 1997), *PLATON* (Spek, 2003), *PRPKAPPA* (Ferguson, 1999).

absence of any significant anomalous scatterers, the value of the Flack (1983) parameter for (3) was inconclusive (Flack & Bernardinelli, 2000) and hence the Friedel equivalents were merged prior to the final refinements.

Supramolecular analyses were performed, and the diagrams were prepared with the aid of *PLATON* (Spek, 2003). Selected molecular dimensions and conformations are given in Table 2, and details of the hydrogen bonding are given in Table 3.<sup>1</sup> Figs. 1–14 show the independent components, with

<sup>1</sup>Supplementary data for this paper, including lists of atomic coordinates, anisotropic displacement parameters, geometric parameters and structure factors, are available from the IUCr electronic archives (Reference: NA5008). Services for accessing these data are described at the back of the journal.

the atom-labelling schemes, and aspects of the supramolecular structures.

### 3. Results and discussion

#### 3.1. Crystallization characteristics and molecular constitutions

The 1:2 adduct, (1), formed between cyclam and adamantane-1-carboxylic acid crystallizes from methanol as a hydrated salt,  $[(cyclam)H_2]^{2+} \cdot [(C_{10}H_{15}COO)^-]_2 \cdot (H_2O)_4$ , in space group  $P2_1/c$ , with  $Z' = 0.5$ . The cation lies across a centre of inversion, selected as that at  $(1, 0, \frac{1}{2})$ , while the other three

**Table 2**  
Selected geometric parameters (Å, °).

| (a) C–N distances in the cations.          |            |  |            |
|--|------------|--|------------|
| (1)  |            |  |            |
| N11–C12                                    | 1.484 (2)  | N14–C13                                    | 1.456 (2)  |
| N11–C17 <sup>a</sup>                       | 1.489 (2)  | N14–C15                                    | 1.468 (2)  |
| (2)  |            |  |            |
| N1–C2                                      | 1.484 (2)  | N4–C3                                      | 1.461 (2)  |
| N1–C7 <sup>b</sup>                         | 1.489 (2)  | N4–C5                                      | 1.470 (2)  |
| (3)  |            |  |            |
| N1–C2                                      | 1.487 (3)  | N4–C3                                      | 1.470 (3)  |
| N1–C14                                     | 1.492 (3)  | N4–C5                                      | 1.466 (3)  |
| N8–C7                                      | 1.496 (3)  | N11–C10                                    | 1.469 (3)  |
| N8–C9                                      | 1.487 (3)  | N11–C12                                    | 1.477 (3)  |
| (4)  |            |  |            |
| N11–C12                                    | 1.496 (3)  | N14–C13                                    | 1.451 (3)  |
| N11–C17 <sup>b</sup>                       | 1.486 (3)  | N14–C15                                    | 1.454 (3)  |
| N21–C22                                    | 1.460 (4)  | N24–C23                                    | 1.479 (4)  |
| N21–C27 <sup>c</sup>                       | 1.522 (4)  | N24–C25                                    | 1.457 (4)  |
| (b) Torsion angles in the cations.         |            |  |            |
| (1)  |            |  |            |
| C17 <sup>a</sup> –N11–C12–C13              | –173.5 (2) | N14–C15–C16–C17                            | –65.7 (2)  |
| N11–C12–C13–N14                            | 66.5 (2)   | C15–C16–C17–N11 <sup>a</sup>               | 68.1 (2)   |
| C12–C13–N14–C15                            | –174.4 (2) | C16–C17–N11 <sup>a</sup> –C12 <sup>a</sup> | –176.0 (2) |
| C13–N14–C15–C16                            | 174.2 (2)  |  |            |
| (2)  |            |  |            |
| C7 <sup>b</sup> –N1–C2–C3                  | –168.8 (2) | N4–C5–C6–C7                                | –63.0 (2)  |
| N1–C2–C3–N4                                | 59.6 (2)   | C5–C6–C7–N1 <sup>b</sup>                   | 69.1 (2)   |
| C2–C3–N4–C5                                | –178.3 (2) | C6–C7–N1 <sup>b</sup> –C2 <sup>b</sup>     | –175.2 (2) |
| C3–N4–C5–C6                                | –179.7 (2) |  |            |
| (3)  |            |  |            |
| C14–N1–C2–C3                               | –170.0 (2) | C7–N8–C9–C10                               | 166.9 (2)  |
| N1–C2–C3–N4                                | 64.5 (3)   | N8–C9–C10–N11                              | –65.4 (3)  |
| C2–C3–N4–C5                                | –174.1 (2) | C9–C10–N11–C12                             | 179.2 (2)  |
| C3–N4–C5–C6                                | 179.2 (2)  | C10–N11–C12–C13                            | –176.7 (2) |
| N4–C5–C6–C7                                | –64.6 (3)  | N11–C12–C13–C14                            | 64.2 (3)   |
| C5–C6–C7–N8                                | 66.8 (3)   | C12–C13–C14–N1                             | –68.5 (3)  |
| C6–C7–N8–C9                                | –171.4 (2) | C13–C14–N1–C2                              | 172.7 (2)  |
| (4)  |            |  |            |
| C17 <sup>b</sup> –N11–C12–C13              | –54.1 (3)  | C27 <sup>c</sup> –N21–C22–C23              | 172.5 (3)  |
| N11–C12–C13–N14                            | –50.1 (3)  | N21–C22–C23–N24                            | –75.2 (3)  |
| C12–C13–N14–C15                            | 176.7 (2)  | C22–C23–N24–C25                            | 173.9 (3)  |
| C13–N14–C15–C16                            | 176.4 (2)  | C23–N24–C25–C26                            | –177.6 (3) |
| N14–C15–C16–C17                            | 55.1 (3)   | N24–C25–C26–C27                            | 66.3 (4)   |
| C15–C16–C17–N11 <sup>b</sup>               | 69.8 (3)   | C25–C26–C27–N21 <sup>c</sup>               | –63.9 (4)  |
| C16–C17–N11 <sup>b</sup> –C12 <sup>b</sup> | 178.9 (2)  | C26–C27–N21 <sup>c</sup> –C22 <sup>c</sup> | 162.3 (3)  |

Symmetry codes: (a)  $2 - x, -y, 1 - z$ ; (b)  $1 - x, 1 - y, 1 - z$ ; (c)  $-x, 1 - y, -z$ .

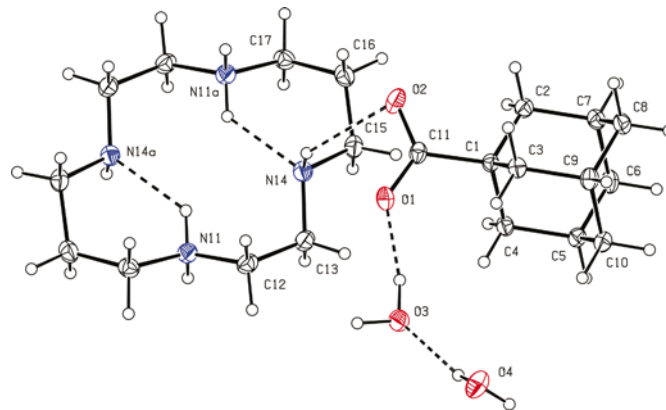
components lie in general positions. In this way, a compact and connected asymmetric unit (Fig. 1) can be specified.

Compound (2), the 1:2 adduct formed between cyclam and 4-aminobenzoic acid, crystallizes from methanol as a hydrated salt,  $[(\text{cyclam})\text{H}_2]^{2+} \cdot [(\text{H}_2\text{NC}_6\text{H}_4\text{COO})^-]_2 \cdot \text{H}_2\text{O}$ , in space group  $C2/c$ , with  $Z' = 0.5$ . The cation lies across a centre of inversion, selected for the sake of convenience as that at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , while the anion lies in a general position. The water molecule lies across a twofold rotation axis, selected as that at  $(\frac{1}{2}, y, \frac{1}{4})$ . In this way, a compact and connected asymmetric unit (Fig. 2) can be specified.

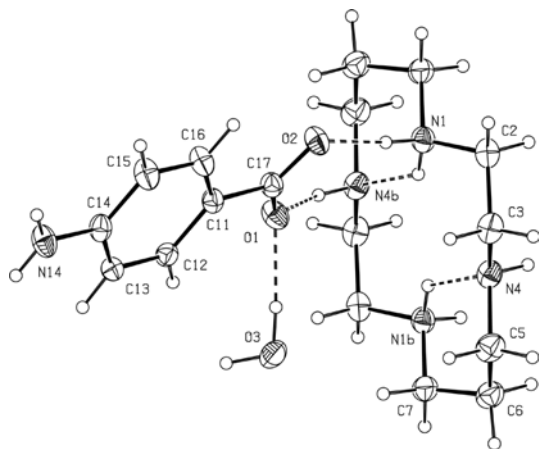
**Table 3**  
Hydrogen-bond parameters (Å, °).

| $D \cdots H \cdots A$              | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|------------------------------------|--------------|--------------|----------------|
| (1)                                |              |              |                |
| O3–H31 $\cdots$ O1 <sup>a</sup>    | 1.75         | 2.689 (2)    | 171            |
| O3–H32 $\cdots$ O1                 | 1.83         | 2.767 (2)    | 168            |
| O4–H41 $\cdots$ O3                 | 2.25         | 3.075 (2)    | 159            |
| O4–H42 $\cdots$ O2 <sup>b</sup>    | 1.83         | 2.688 (2)    | 171            |
| N11–H11A $\cdots$ O3 <sup>c</sup>  | 1.92         | 2.792 (2)    | 158            |
| N11–H11B $\cdots$ N14 <sup>d</sup> | 2.13         | 2.818 (2)    | 131            |
| N14–H14A $\cdots$ O2               | 2.55         | 3.270 (2)    | 136            |
| (2)                                |              |              |                |
| O3–H3 $\cdots$ O1                  | 1.79         | 2.737 (2)    | 171            |
| N1–H1A $\cdots$ O2                 | 1.77         | 2.688 (2)    | 175            |
| N1–H1B $\cdots$ N4 <sup>e</sup>    | 2.13         | 2.847 (2)    | 134            |
| N4–H4 $\cdots$ O1 <sup>a</sup>     | 2.29         | 3.111 (2)    | 148            |
| N14–H14A $\cdots$ O2 <sup>e</sup>  | 2.16         | 3.022 (2)    | 167            |
| N14–H14B $\cdots$ O2 <sup>f</sup>  | 2.13         | 2.916 (2)    | 148            |
| C2–H2B $\cdots$ O3 <sup>a</sup>    | 2.54         | 3.409 (2)    | 146            |
| C7–H7B $\cdots$ O3                 | 2.39         | 3.295 (2)    | 152            |
| (3)                                |              |              |                |
| O1–H11 $\cdots$ O2                 | 1.94         | 2.776 (3)    | 171            |
| O1–H12 $\cdots$ O22                | 1.92         | 2.754 (3)    | 176            |
| O2–H21 $\cdots$ O31 <sup>g</sup>   | 1.89         | 2.714 (3)    | 167            |
| O2–H22 $\cdots$ O32                | 2.02         | 2.835 (3)    | 163            |
| O23–H23 $\cdots$ O21 <sup>h</sup>  | 1.84         | 2.674 (3)    | 171            |
| O33–H33 $\cdots$ O1 <sup>b</sup>   | 1.83         | 2.660 (3)    | 168            |
| N1–H1A $\cdots$ O21                | 1.82         | 2.729 (3)    | 169            |
| N1–H1B $\cdots$ N11                | 2.10         | 2.839 (3)    | 137            |
| N4–H4 $\cdots$ O31                 | 2.25         | 3.114 (3)    | 155            |
| N8–H8A $\cdots$ N4                 | 2.11         | 2.848 (3)    | 136            |
| N8–H8B $\cdots$ O32 <sup>j</sup>   | 1.85         | 2.767 (3)    | 177            |
| N11–H11A $\cdots$ O22 <sup>k</sup> | 2.20         | 3.035 (3)    | 150            |
| (4)                                |              |              |                |
| O5–H5 $\cdots$ O2 <sup>l</sup>     | 1.72         | 2.560 (2)    | 174            |
| O6–H6A $\cdots$ O4                 | 2.00         | 2.827 (3)    | 169            |
| N11–H11A $\cdots$ O1 <sup>m</sup>  | 1.95         | 2.801 (2)    | 154            |
| N11–H11B $\cdots$ O4               | 1.91         | 2.818 (2)    | 169            |
| N21–H21A $\cdots$ N24 <sup>n</sup> | 1.98         | 2.752 (3)    | 140            |
| N21–H21B $\cdots$ O3               | 1.86         | 2.690 (3)    | 149            |
| N24–H24 $\cdots$ O2 <sup>n</sup>   | 2.36         | 3.222 (3)    | 155            |

Symmetry codes: (a)  $1 - x, 1 - y, 1 - z$ ; (b)  $-1 + x, y, z$ ; (c)  $1 - x, -y, 1 - z$ ; (d)  $2 - x, -y, 1 - z$ ; (e)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (f)  $x, 2 - y, -\frac{1}{2} + z$ ; (g)  $x, -y, -\frac{1}{2} + z$ ; (h)  $x, 1 - y, -\frac{1}{2} + z$ ; (i)  $x, -y, \frac{1}{2} + z$ ; (j)  $x, 1 - y, \frac{1}{2} + z$ ; (l)  $x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (m)  $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (n)  $-x, 1 - y, -z$ .

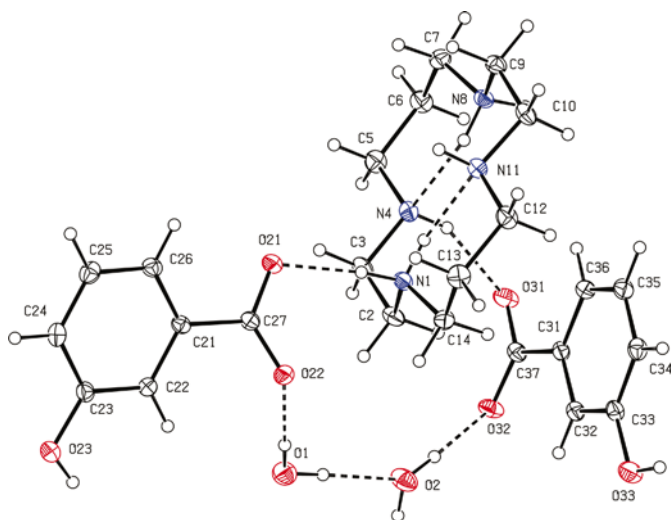


**Figure 1**  
The independent components of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The cation depicted lies across a centre of inversion, and atoms marked 'a' are at the symmetry position  $(2 - x, -y, 1 - z)$ .

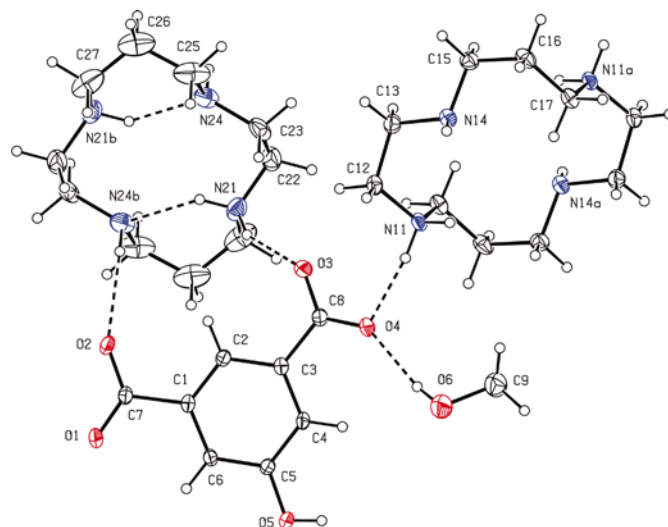


**Figure 2**  
The independent components of (2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The cation depicted lies across a centre of inversion, and atoms marked 'b' are at the symmetry position  $(1 - x, 1 - y, 1 - z)$ .

The 1:2 adduct, (3), formed between cyclam and 3-hydroxybenzoic acid upon crystallization from methanol is a hydrated salt,  $[\{(\text{cyclam})\text{H}_2\}^{2+}] \cdot [(\text{HOC}_6\text{H}_4\text{COO})^-]_2 \cdot (\text{H}_2\text{O})_2$ , and all five molecular components lie in general positions in the non-centrosymmetric space group  $Pc$ , with  $Z' = 1$ . The independent components are linked into a three-dimensional framework by a very extensive series of hydrogen bonds (Table 3), ten of which are formed between different molecular units. Nonetheless, it is possible to select a compact asymmetric unit (Fig. 3) where, in addition to the usual pair of  $\text{N}-\text{H} \cdots \text{N}$  hydrogen bonds within the  $[(\text{cyclam})\text{H}_2]^{2+}$  cation, there are five hydrogen bonds linking the components within the asymmetric unit, thus leaving another five hydrogen bonds available to link the five-component aggregates into the overall framework.



**Figure 3**  
The independent components of (3), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 4**  
The independent components of (4), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The cations depicted lie across centres of inversion, and atoms marked 'a' or 'b' are at the symmetry positions  $(1 - x, 1 - y, 1 - z)$  and  $(-x, 1 - y, -z)$ , respectively.

Compound (4) is a solvated salt,  $[\{(\text{cyclam})\text{H}_2\}^{2+}] \cdot \text{forcelb}[\{(\text{HOC}_6\text{H}_4(\text{COO})_2\}^-] \cdot \text{CH}_3\text{OH}$ , where the solvent component is methanol, unlike compounds (1)–(3), which are all hydrated salts. Two H atoms have been fully transferred from the two carboxyl groups to the cyclam unit. The anion and the methanol molecule lie in general positions in space group  $P2_1/c$ , while there are two independent cations lying across centres of inversion, selected as those at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  for cation 1 (containing atoms N11 and N14) and  $(0, \frac{1}{2}, 0)$  for cation 2 (containing atoms N21 and N24). The asymmetric unit thus comprises two half cations, one anion and one neutral methanol molecule (Fig. 4).

### 3.2. Molecular conformations and dimensions

The cations in (1), (2) and (4) are centrosymmetric, and that in (3) adopts a conformation that is almost centrosymmetric. The cations in (1), (2) and (3) all adopt a *trans*-III configuration<sup>2</sup> (Barefield *et al.*, 1986), with almost perfect staggering about all of the C–C and C–N bonds (Table 2). It is noteworthy that in (3), the corresponding torsion angles in the sequences from atom C14 *via* atom N4 to atom C9, and from atom C7 *via* atom N11 to atom C2, are of very similar magnitude but with opposite signs in every pair, indicative of the approximate centrosymmetry. There are paired  $\text{N}-\text{H} \cdots \text{N}$  hydrogen bonds within each of these cations (Table 3 and Figs. 1–3) and two  $\text{N}-\text{H}$  bonds on each face of the disk-like

<sup>2</sup> In the centrosymmetric *trans*-III form, the configurations at atoms N1 and N4 are (*R,R*), with the corresponding axial  $\text{N}-\text{H}$  bonds on opposite faces of the macrocycle. In the centrosymmetric *trans*-IV form, the configurations at atoms N1 and N4 are (*R,S*), with the corresponding axial  $\text{N}-\text{H}$  bonds on the same face of the macrocycle. In the corresponding non-centrosymmetric forms, the configurations at atoms N1, N4, N8 and N11 are (*R,R,S,S*) for *trans*-III and (*R,S,S,R*) for *trans*-IV.

macrocycle, which are available for the formation of exterior hydrogen bonds

Although both of the cations in (4) are centrosymmetric, they have significantly different conformations. In cation 2, the skeletal torsion angles in the fragment from atom C27<sup>i</sup> [symmetry code: (i)  $-x, 1 - y, -z$ ] via atoms N21 and N24 to atom C22<sup>i</sup> follow the sequence *ap, sc, ap, ap, sc, sc, ap* (where *ap* and *sc* denote antiperiplanar and synclinal, respectively), *i.e.* this cation has the *trans*-III configuration, while the corresponding series of torsion angles in cation 1 follows the sequence *sc, sc, ap, ap, sc, sc, ap*, and this cation approximates to the *trans*-IV configuration. However, only cation 2 contains the usual paired intramolecular N—H···N hydrogen bonds (Table 3 and Fig. 4).

In the cations of (1)–(3), and in the type 1 cation of (4), the C—N distances associated with protonated N atoms are consistently and significantly longer than those associated with non-protonated N atoms, and in each cation, the ranges spanned by the two types of distance are small, usually no more than 0.01 Å (Table 2). However, for the type 2 cation in (4), the two independent C—N distances involving the protonated atom N21 differ by ~0.06 Å, while those associated with the unprotonated atom N24 differ by ~0.02 Å.

The dimensions of the anions present no unusual features.

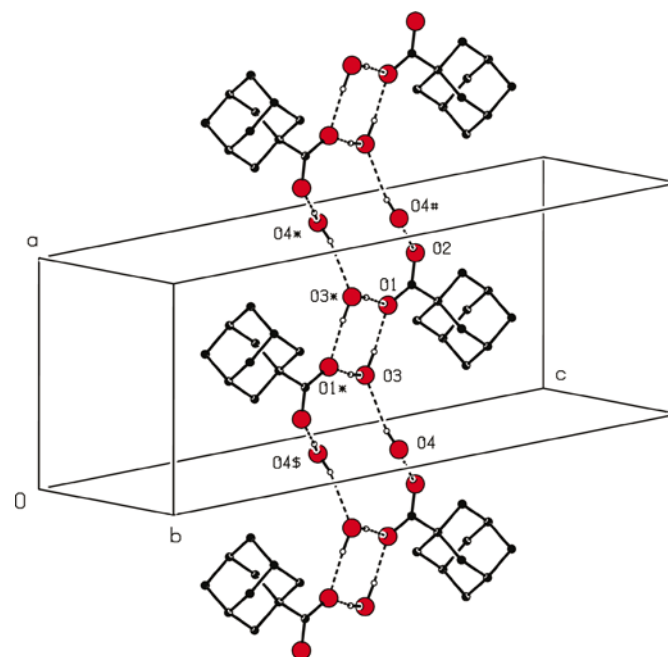
### 3.3. Supramolecular structures

In each of (1)–(4), an extensive range of hydrogen bonds (Table 3) contribute to the formation of the supramolecular structures. With the exception of the water and methanol solvent molecules, the components of (1)–(4) are all charged, leading to the development of charge-assisted hydrogen bonding (Gilli *et al.*, 1994). The majority of the hydrogen bonds are of O—H···O and N—H···O types, but there are also N—H···N hydrogen bonds within most of the cations.

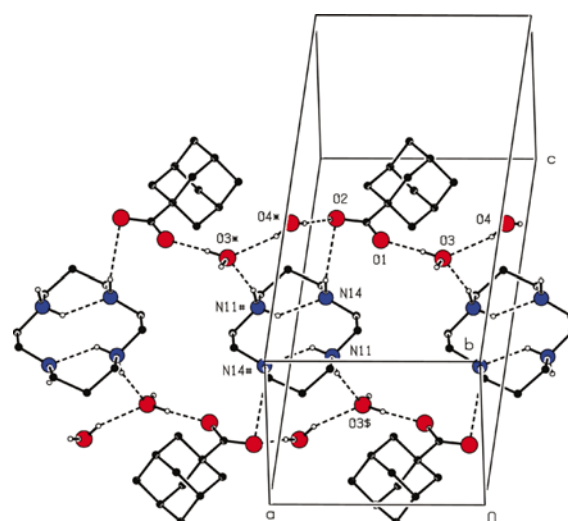
**3.3.1. Compound (1).** The independent components in (1) are linked into a two-dimensional structure by the hydrogen bonds (Table 3), of which four lie within the selected asymmetric unit. In addition to an intracation N—H···N hydrogen bond, which forms a centrosymmetric  $R_2^2(10)$  motif, water atoms O3 and O4 act as hydrogen-bond donors, *via* atoms H32 and H41, respectively, to atoms O1 and O3, and atom N14 also acts as a donor, *via* atom H14A, to atom O2 (Fig. 1). There are thus three hydrogen bonds that link the seven-component aggregates, and the action of these bonds is most simply analysed using the substructure approach (Gregson *et al.*, 2000). The anions and the water molecules together form molecular ladders along [100], and these ladders are linked by the cations into (001) sheets.

Water atom O4 at  $(x, y, z)$  acts as a hydrogen-bond donor, *via* H42, to carboxylate atom O2 at  $(-1 + x, y, z)$ ; this bond, in combination with the O—H···O hydrogen bonds within the asymmetric unit, generates by translation a  $C_3^3(8)$  chain running parallel to the [100] direction (Fig. 5). Water atom O3 at  $(x, y, z)$  acts as a donor, *via* H31, to carboxylate atom O1 at  $(1 - x, 1 - y, 1 - z)$ , which lies in an antiparallel [100] chain that is related to the initial [100] chain by the action of

inversion centres. Propagation of these O—H···O hydrogen bonds by translation and inversion thus generates a chain of fused centrosymmetric rings, with  $R_4^2(8)$  rings centred at  $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  ( $n = \text{zero or integer}$ ) alternating with  $R_6^0(16)$  rings centred at  $(n, \frac{1}{2}, \frac{1}{2})$  ( $n = \text{zero or integer}$ ). This substructure may alternatively be regarded as a molecular ladder, in which an anti-



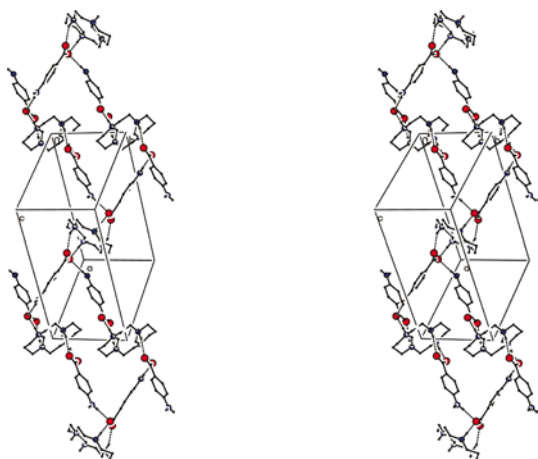
**Figure 5** Part of the crystal structure of (1), showing the formation, by the anions and water molecules only, of a molecular ladder along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (\*), a hash (#) or a dollar sign (\$) are at the symmetry positions  $(1 - x, 1 - y, 1 - z)$ ,  $(1 + x, y, z)$  and  $(-x, 1 - y, 1 - z)$ , respectively.



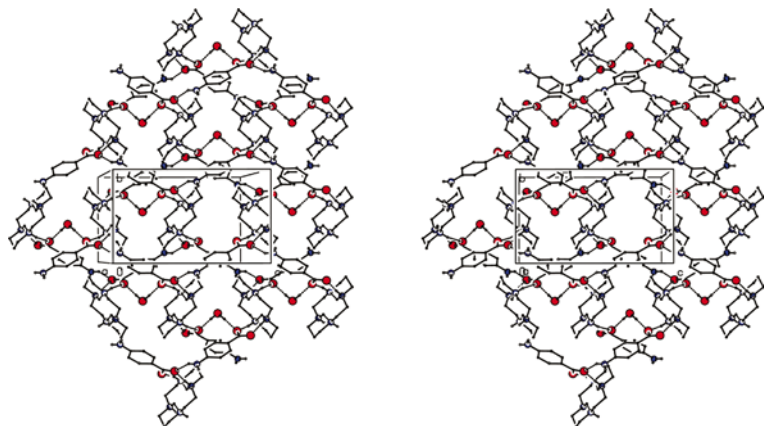
**Figure 6** Part of the crystal structure of (1), showing the linking by the cations of the ladders along  $(x, \frac{1}{2}, \frac{1}{2})$  and  $(x, -\frac{1}{2}, \frac{1}{2})$  to form part of a (001) sheet. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (\*), a hash (#) or a dollar sign (\$) are at the symmetry positions  $(1 + x, y, z)$ ,  $(2 - x, -y, 1 - z)$  and  $(1 - x, -y, 1 - z)$ , respectively.

parallel pair of  $C_3^2(8)$  chains forms the uprights and the paired  $O3-H31 \cdots O1^i$  [symmetry code: (i)  $1-x, 1-y, 1-z$ ] hydrogen bonds form the rungs. Two of these ladders run through each unit cell, one lying along the line  $(x, \frac{1}{2}, \frac{1}{2})$  and the other lying along the line  $(x, 0, 0)$ .

Each cation acts as a donor in four  $N-H \cdots O$  hydrogen bonds, in which the acceptors are two carboxylate O atoms and two water O atoms. In the cation centred at  $(1, 0, \frac{1}{2})$ , atom N11 at  $(2-x, -y, 1-z)$  and atom N14 at  $(x, y, z)$  act as hydrogen-bond donors to atom O3 at  $(1+x, y, z)$  and to atom O2 at  $(x, y, z)$ , respectively, both of which lie in the molecular ladder along  $(x, \frac{1}{2}, \frac{1}{2})$ , while in the same cation, the symmetry-related atoms N11 at  $(x, y, z)$  and N14 at  $(2-x, -y, 1-z)$  act as donors, respectively, to atoms O3 at  $(1-x, -y, 1-z)$  and O2 at  $(2-x, -y, 1-z)$ , which both lie in the ladder along  $(x, -\frac{1}{2}, \frac{1}{2})$ . Propagation of these  $N-H \cdots O$  interactions thus generates a (001) sheet (Fig. 6); the overall structure is defined by two such sheets, related to each other by the action of the glide planes, with one in the domain  $0.26 < z < 0.74$  and the



**Figure 7**  
A stereoview of part of the crystal structure of (2), showing the formation of a  $(10\bar{1})$  sheet. For the sake of clarity, water molecules and H atoms bonded to C atoms have been omitted.



**Figure 8**  
A stereoview of part of the crystal structure of (2), showing two interwoven  $(100)$  sheets linked by water molecules. For the sake of clarity, H atoms bonded to C atoms have been omitted.

other in the domain  $-0.24 < z < 0.24$ , but there are no direction-specific interactions between adjacent sheets.

**3.3.2. Compound (2).** In (2), the components are linked into a three-dimensional framework by hydrogen bonds (Table 3), and of the six structurally significant hydrogen bonds, four lie within the specified asymmetric unit. Atoms N1 at  $(x, y, z)$  and N4 at  $(1-x, 1-y, 1-z)$ , *i.e.* N atoms separated by a  $-(CH_2)_3-$  unit that have axial  $N-H$  bonds on the same face of the macrocycle, act as hydrogen-bond donors to atoms O2 and O1, respectively. This interaction provides a multi-point linking of the cation and the anion, which is analogous to those observed in  $[Ni(cyclam)^{2+}]$  complexes with carboxylate anions (Zakaria *et al.*, 2002). In addition, atom N1 at  $(x, y, z)$  forms the usual intramolecular  $N-H \cdots N$  hydrogen bond to atom N4 at  $(1-x, 1-y, 1-z)$ . There is thus an  $R_2^2(10)$  hydrogen-bond motif within the cation, flanked on either side by an  $R_3^3(8)$  ring involving both cation and anions (Fig. 2). Water molecule O3 at  $(x, y, z)$  acts as a hydrogen-bond donor to atoms O1 in the anions at  $(x, y, z)$  and  $(1-x, y, \frac{1}{2}-z)$ . Propagation by the centre of inversion at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  of the hydrogen bonds within the asymmetric unit generates a neutral five-component aggregate, in which there are four amine  $N-H$  bonds and two water  $O-H$  bonds still available for hydrogen-bond formation between these aggregates.

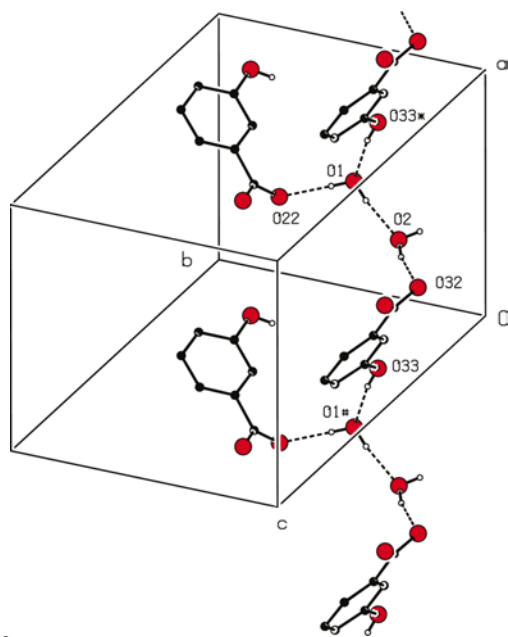
The formation of the three-dimensional framework is most readily analysed in terms of the effect of each of the three distinct external hydrogen bonds that link the aggregates. Amine atoms N14 at  $(x, y, z)$  and  $(1-x, 1-y, 1-z)$  both lie in the aggregate centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . Each of these atoms acts as a hydrogen-bond donor, *via* H14A, to atoms O2 in the anions at  $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$  and  $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ , respectively, which themselves lie in the aggregates centred at  $(0, 1, 0)$  and  $(1, 0, 1)$ , respectively. Atoms O2 at  $(x, y, z)$  and  $(1-x, 1-y, 1-z)$  accept similar hydrogen bonds from atoms N14 at  $(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$  and  $(\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z)$ , respectively, which lie in the aggregates centred at  $(0, 0, 0)$  and  $(1, 1, 1)$ , respectively. Hence the single  $N-H \cdots O$  hydrogen bond involving atom H14A (Table 3) links the aggregate centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  with those centred at  $(0, 0, 0)$ ,  $(0, 1, 0)$ ,  $(1, 0, 1)$  and  $(1, 1, 1)$ , and propagation of these links by the space group generates a  $(10\bar{1})$  sheet built from a single type of  $R_8^6(46)$  ring (Fig. 7).

The two N14 atoms in the aggregate at  $(x, y, z)$  and  $(1-x, 1-y, 1-z)$  also act as hydrogen-bond donors, this time *via* H14B, to atoms O2 at  $(x, 2-y, -\frac{1}{2}+z)$  and  $(1-x, -1+y, \frac{3}{2}-z)$ , respectively, which are components of the aggregates centred at  $(\frac{1}{2}, \frac{3}{2}, 0)$  and  $(\frac{1}{2}, -\frac{1}{2}, 1)$ , respectively. Atoms O2 at  $(x, y, z)$  and  $(1-x, 1-y, 1-z)$  accept similar hydrogen bonds from atoms N14 at  $(x, 2-y, \frac{1}{2}+z)$  and  $(1-x, -1+y, \frac{1}{2}-z)$ , which are components of the aggregates centred at  $(\frac{1}{2}, \frac{3}{2}, 1)$  and  $(\frac{1}{2}, -\frac{1}{2}, 0)$ , respectively. Propagation of these links generates a deeply puckered  $(100)$  sheet (Fig. 8) that lies in the domain  $0.26 < x < 0.74$  and in which the repeat along  $[010]$  is two unit-cell vectors. Four such sheets are thus required to complete the structure; two sheets in the

domain  $0.26 < x < 0.74$  are mutually interwoven (Fig. 8), and there is a second interwoven pair in the domain  $0.76 < x < 1.24$ , related to the first pair by the action of the  $C$ -centring operation. Within each domain, the pairs of puckered sheets are linked by the water molecules. Water atom O3 at  $(\frac{1}{2}, y, \frac{1}{4})$  acts as a hydrogen-bond donor to carboxylate atoms O1 in the anions at  $(x, y, z)$  and  $(1 - x, y, \frac{1}{2} - z)$ , which lie in different sheets of the interwoven pair. Water atom O3 is not an acceptor of hard hydrogen bonds but acts as an acceptor in two  $C-H \cdots O$  hydrogen bonds, both within the five-component aggregate (Table 3).

The combination of the pairwise interwoven (100) sheets (Fig. 8) and the  $(10\bar{1})$  sheets (Fig. 7) is sufficient to generate a single three-dimensional framework.

**3.3.3. Compound (3).** Within the asymmetric unit of (3) (Fig. 3), atoms N1 and N4 act as hydrogen-bond donors to carboxylate atoms O21 and O31, respectively. Water atom O1 acts as a donor, *via* H11 and H12, to water atom O2 and carboxylate atom O22, respectively, and water atom O2 in turn acts as a donor, *via* H22, to carboxylate atom O32. The hydrogen-bond donors available for the formation of external links between the five-component aggregates are thus atoms N8, N11 and O2 (*via* H21) and hydroxy atoms O23 and O33. The resulting framework is most simply analysed by use of the substructure approach. The anions and the water molecules alone give rise to readily identifiable substructures in one and two dimensions, which together generate the three-dimensional framework without any involvement of the cations. A simple one-dimensional motif can be identified, which involves just the type 2 anion and the two water molecules; hydroxy atom O33 at  $(x, y, z)$  acts as a hydrogen-bond donor



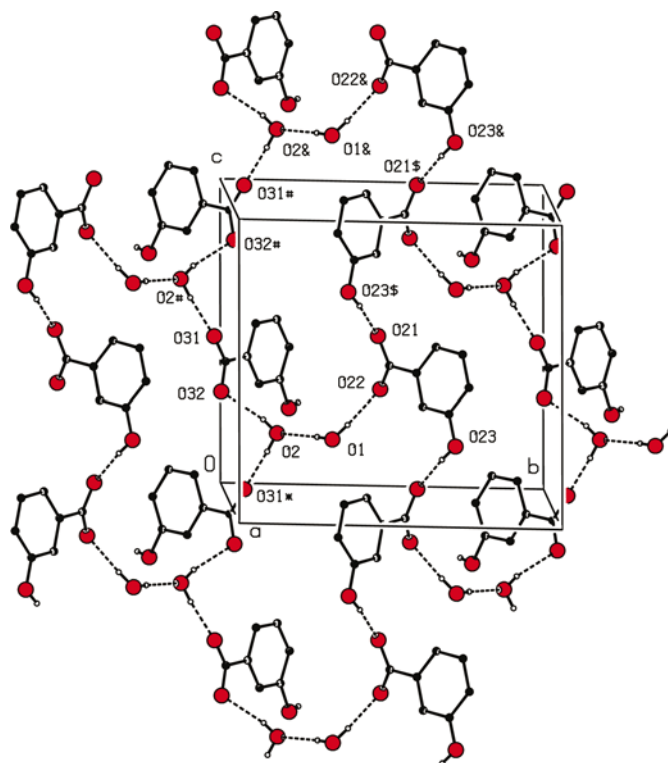
**Figure 9**

Part of the crystal structure of (3), showing the formation of a  $C_3^3(11)$  chain of type 2 anions and water molecules, with pendent type 1 anions, parallel to  $[100]$ . For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (\*) are at the symmetry position  $(-1 + x, y, z)$ .

to water atom O1 at  $(-1 + x, y, z)$ , so generating by translation a  $C_3^3(11)$  chain running parallel to the  $[100]$  direction, from which the type 1 anions are pendent (Fig. 9). Two chains of this type run through each unit cell, one in the domain  $0 < y < \frac{1}{2}$ ,  $0 < z < \frac{1}{2}$  and the other in the domain  $\frac{1}{2} < y < 1.0$ ,  $\frac{1}{2} < z < 1.0$ .

Two further one-dimensional motifs, both of which are chains parallel to the  $[001]$  direction, combine to generate a (100) sheet containing both anions and both water molecules. Hydroxy atom O23 at  $(x, y, z)$  acts as a hydrogen-bond donor to carboxylate atom O21 at  $(x, 1 - y, -\frac{1}{2} + z)$ , so producing a  $C(7)$  chain along  $[001]$  containing a single anionic species and generated by the  $c$ -glide plane at  $y = \frac{1}{2}$ . Water atom O2 at  $(x, y, z)$  acts as a donor, *via* H21, to carboxylate atom O31 at  $(x, -y, -\frac{1}{2} + z)$ , so giving a second  $[001]$  chain, this time of  $C_2^2(6)$  type, involving both an anion and a water molecule and generated by the  $c$ -glide plane at  $y = 0$ . These two  $[001]$  chains are connected by the water molecule containing atom O1 (Table 3 and Fig. 3), giving (100) sheets built from a single type of  $R_{10}^{10}(36)$  ring (Fig. 10).

The linking of the (100) sheets by the  $[100]$  chains generates a three-dimensional framework built from anions and water molecules only, which encapsulates voids representing 50% of the total volume (Fig. 11). The  $[(cyclam)H_2]^{2+}$  cation is linked to this framework by four  $N-H \cdots O$  hydrogen bonds (Table 3), such that each anion is linked to four different anions. Atoms N1 and N4 act as hydrogen-bond donors to



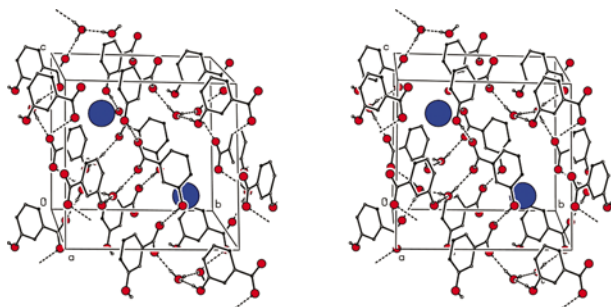
**Figure 10**

Part of the crystal structure of (3), showing the formation of a (100) sheet of  $R_{10}^{10}(36)$  rings built from anions and water molecules only. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (\*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions  $(x, -y, -\frac{1}{2} + z)$ ,  $(x, -y, \frac{1}{2} + z)$ ,  $(x, 1 - y, \frac{1}{2} + z)$  and  $(x, y, 1 + z)$ , respectively.

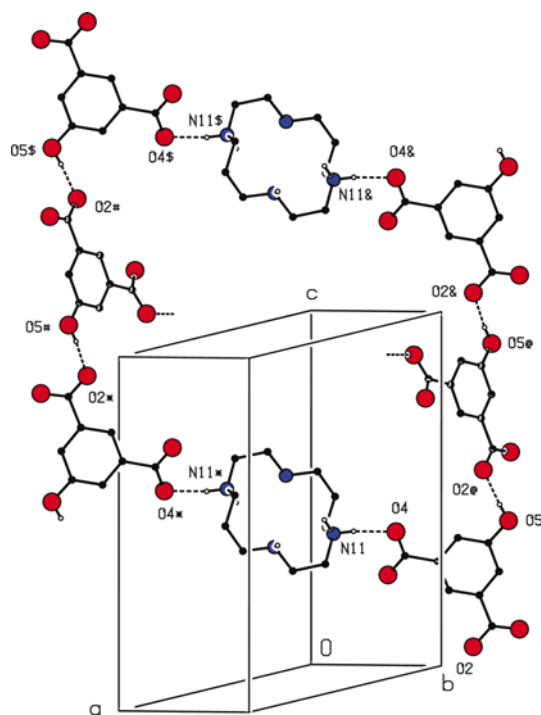


carboxylate atoms O21 and O31, respectively, within the asymmetric unit, and atoms N8 and N11 act as donors, respectively, to carboxylate atoms O32 at  $(x, -y, \frac{1}{2} + z)$  and O22 at  $(x, 1 - y, \frac{1}{2} + z)$ . All of these carboxylate O acceptors are components of anions lying in a single (100) sheet, and the pattern of these N—H...O hydrogen bonds, involving all four carboxylate O atoms, is sufficient to preclude the possibility of any additional symmetry.

**3.3.4. Compound (4).** In addition to the paired N—H...N hydrogen bonds within cation 2 of (4), six other hard hydrogen bonds are present, which link the individual molecular components into a three-dimensional framework. Four of



**Figure 11**  
A stereoview of part of the crystal structure of (3), showing one of the voids in the three-dimensional anion–water framework. For the sake of clarity, H atoms bonded to C atoms have been omitted. Large spheres indicate the positions of the cation centroids.



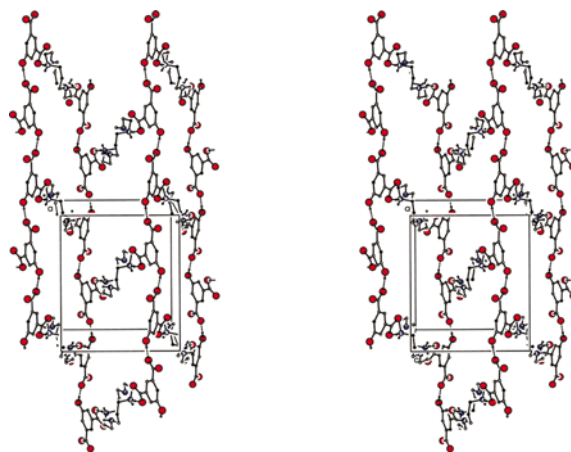
**Figure 12**  
Part of the crystal structure of (4), showing the formation of one of the  $R_8^s(62)$  rings, containing only anions and type 1 cations, that form the (100) sheet. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (\*), a hash (#), a dollar sign (\$), an ampersand (&) or an at sign (@) are at the symmetry positions  $(1 - x, 1 - y, 1 - z)$ ,  $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ ,  $(1 - x, 1 - y, 2 - z)$ ,  $(x, y, 1 + z)$  and  $(x, \frac{3}{2} - y, \frac{1}{2} + z)$ , respectively.

these hydrogen bonds occur within the selected asymmetric unit, leaving just two hydrogen bonds exterior to the asymmetric unit (Fig. 4).

The three-dimensional framework is readily analysed by means of the substructure approach. The anions alone form chains along the [001] direction; these chains in combination with the type 1 cations give (100) sheets; and the combination of these sheets with the type 2 cations yields the complete framework. The methanol molecules act as hydrogen-bond donors, but not as acceptors, and are thus simply pendent from the framework without being an integral part of its construction. It is indeed possible that the primary role of the methanol molecules is to act as space fillers.

The anion chain involves a single hydrogen bond. Hydroxy atom O5 in the anion at  $(x, y, z)$  acts as a hydrogen-bond donor to carboxylate atom O2 at  $(x, \frac{3}{2} - y, \frac{1}{2} + z)$ , so producing a  $C(7)$  chain running parallel to [001] and generated by the  $c$ -glide plane at  $y = \frac{3}{4}$  (Fig. 12). This chain lies in the domain  $0.60 < y < 0.90$ , and a second (antiparallel) chain, which is related to the first by the action of centres of inversion and is generated by the glide plane at  $y = \frac{1}{4}$ , lies in the domain  $0.10 < y < 0.40$ . Cations of type 1 link the [001] chains. In the cation centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , atoms N1 at  $(x, y, z)$  and  $(1 - x, 1 - y, 1 - z)$  act as hydrogen-bond donors, *via* H11B, to carboxylate atom O4 in the anions at  $(x, y, z)$  and  $(1 - x, 1 - y, 1 - z)$ , respectively, which themselves form parts of the chains generated by the glide planes at  $y = \frac{3}{4}$  and  $y = \frac{1}{4}$ . In a similar way, the type 1 cation centred at  $(\frac{1}{2}, 1, 1)$  acts as a hydrogen-bond donor to atoms O4 in the anions at  $(x, \frac{3}{2} - y, \frac{1}{2} + z)$  and  $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ , which are components of [001] chains generated by glide planes at  $y = \frac{3}{4}$  and  $y = \frac{1}{4}$ , respectively. In this manner, each [001] chain is linked to the two adjacent chains along the [010] direction, so forming a deeply puckered (100) sheet built from a single type of  $R_8^s(62)$  ring (Figs. 12 and 13).

Adjacent (100) sheets are linked by the type 2 cations. Atoms N21 at  $(x, y, z)$  and  $(-x, 1 - y, -z)$ , which are



**Figure 13**  
A stereoview of part of the crystal structure of (4), showing the formation of a (100) sheet built from anions and type 1 cations only. For the sake of clarity, H atoms bonded to C atoms have been omitted.



#### 4. Concluding comments

Solvated salt-type adducts of cyclam with carboxylic acids form a rich variety of hydrogen-bonded supramolecular structures in two or three dimensions. It is striking that, although the tet-a analogues generally have similar compositions and similar constitutions, their crystallization characteristics, as defined by the space groups and  $Z'$  values, and the patterns of supramolecular aggregation are entirely different for corresponding pairs of cyclam and tet-a salts. This fact points to unexpected subtleties in the effects of the hexa-C-methylation that defines the difference between cyclam and tet-a, which may not be readily amenable to predictive computation. Likewise, the concurrent occurrence of two configurational forms of the  $[(\text{cyclam})\text{H}_2]^{2+}$  cation in (4) is unexpected and indicates that the direction-specific contribution to the total inter-ionic interaction energy may be sufficient to tilt the balance between one isomer and another.

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