Hydrated salts of 3,5-dihydroxybenzoic acid with organic diamines: hydrogen-bonded supramolecular structures in two and three dimensions

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The trigonally trisubstituted acid 3,5-dihydroxybenzoic acid forms hydrated salt-type adducts with organic diamines. In 1,4-diazabicyclo[2.2.2]octane–3,5-dihydroxybenzoic acid–water (1/1/1) (1), where $Z' = 2$ in $P2_1/c$, the constitution is $[HN(CH_2CH_2)_3N]^+ \cdot [(HO)_2C_6H_3COO]^- \cdot H_2O$: the anions and the water molecules are linked by six O—H$\cdots$O hydrogen bonds to form two-dimensional sheets and each cation is linked to a single sheet by one O—H$\cdots$N and one N—H$\cdots$O hydrogen bond. Piperazine–3,5-dihydroxybenzoic acid–water (1/2/4) (2) and 1,2-diaminoethane–3,5-dihydroxybenzoic acid–water (1/2/2) (3) are also both salts with constitutions $[H_2N(CH_2CH_2)_2NH_2]^{2+} \cdot 2[(HO)_2C_6H_3COO]^- \cdot 4H_2O$ and $[H_3NCH_2CH_2NH_3]^{2+} \cdot 2[(HO)_2C_6H_3COO]^- \cdot 2H_2O$, respectively. Both (2) and (3) have supramolecular structures which are three-dimensional: in (2) the anions and the water molecules are linked by six O—H$\cdots$O hydrogen bonds to form a three-dimensional framework enclosing large centrosymmetric voids, which contain the cations that are linked to the framework by two N—H$\cdots$O hydrogen bonds; in (3) the construction of the three-dimensional framework requires the participation of cations, anions and water molecules, which are linked together by four O—H$\cdots$O and three N—H$\cdots$O hydrogen bonds.

1. Introduction

The trigonally trisubstituted aromatic acid 3,5-dihydroxybenzoic acid (I) is potentially an extremely versatile building block for supramolecular synthesis. It has three substituents carried on a rigid, planar platform, each of which is capable of acting as both a hydrogen-bond donor and as a hydrogen-bond acceptor. The mutual disposition of these three substituents is designed to preclude any intramolecular hydrogen bonding. This acid has already been utilized in supramolecular chemistry, in the formation of a pillared-layer framework structure with the tetra-aza macrocycle *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($C_{16}H_{36}N_4$, tet-a; Gregson *et al.*, 2000): in this 1:2 salt the $[(HO)_2C_6H_3COO]^-$ anions form hydrogen-bonded sheets which are held together by the $[C_{16}H_{38}N_4]^{2+}$ cations, while in the salt formed with bis(2-aminoethyl)amine, the anions form a three-dimensional framework (Glidewell, Ferguson, Gregson & Campana, 2000). On the other hand, with the simple diamine 4,4'-bipyridyl there is no proton transfer from acid to base and the acid molecules behave as triple donors of hydrogen bonds generating a simple chain of rings (Wheatley *et al.*, 1999), closely similar to that formed by the related trigonally substituted precursor 1,3,5-trihydroxybenzene with 4,4'-bipyridyl (Coupar *et al.*, 1996).

Developing the use of this building block, we have now made a study of its adducts formed with a range of simple diamines (II)–(VI),
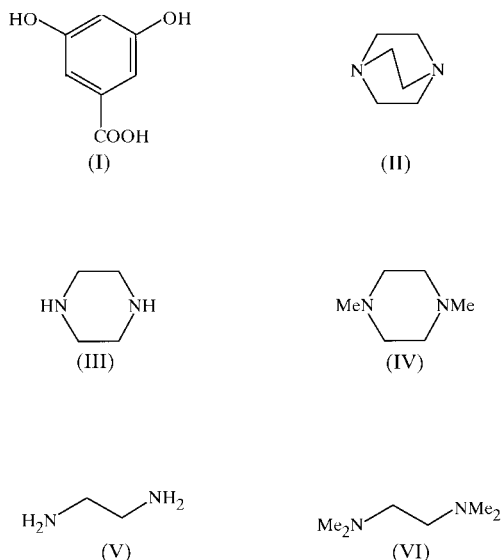
whose common feature is the N—C—C—N linkage containing two N atoms, capable of acting either as hydrogen-bond acceptors or as proton acceptors and thence as hydrogen-bond donors, which are separated by a two-atom linked unit. The diamines (II), (III) and (V) are respectively tertiary, secondary and primary amines, expected when protonated to form an increasingly complex range of N—H···O hydrogen bonds: the diamines (IV) and (VI) have the same skeletons as (III) and (V), respectively, but both are tertiary amines. Thus, the diamines (II), (IV) and (VI) form another series of tertiary amines which are respectively bicyclic, monocyclic and acyclic.

We have now synthesized three hydrated adducts whose crystal structures are reported here: 1,4-diazabicyclo[2.2.2]octane–3,5-dihydroxybenzoic acid–water (1/1/1) (1), where the supramolecular structure is two-dimensional; piperazine–3,5-dihydroxybenzoic acid–water (1/2/4) (2) and 1,2-diaminoethane–3,5-dihydroxybenzoic acid–water (1/2/2) (3), both of which have three-dimensional structures. We have also prepared a series of anhydrous adducts (4)–(7) from the diamines (II)–(V) respectively, and a hydrate (8) from (VI), but in none of these examples were any crystals obtained which proved to be suitable for single-crystal X-ray diffrac-
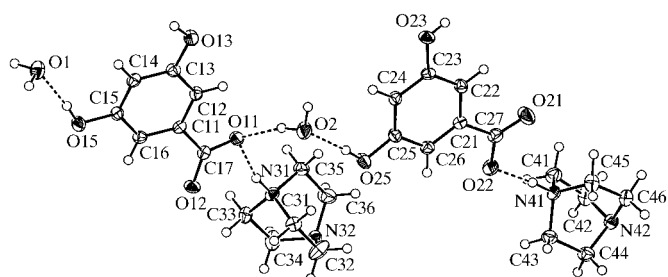
tion. In each of (1)–(3), the water molecules are intimately bound into the supramolecular structure.

2. Experimental

2.1. Synthesis

Stoichiometric quantities of 3,5-dihydroxybenzoic acid and the appropriate diamine were separately dissolved in anhydrous methanol: these solutions were mixed to give a molar ratio amine:acid of 1:2 and the mixtures were then set aside to crystallize, producing analytically pure samples of (4)–(8). Analyses: (4) found C 57.0, H 5.7, N 6.6%; $C_{20}H_{24}N_2O_8$ requires C 57.1, H 5.8, N 6.7%; (5) found C 54.8, H 5.6, N 7.1%; $C_{18}H_{22}N_2O_8$ requires C 54.8, H 5.6, N 7.1%; (6) found C 56.9, H 6.2, N 6.6%; $C_{20}H_{26}N_2O_8$ requires C 56.9, H 6.2, N 6.6%; (7) found C 51.8, H 5.5, N 7.6%; $C_{16}H_{20}N_2O_8$ requires C 52.2, H 5.5, N 7.6%; (8) found C 53.8, H 6.7, N 6.2%; $C_{20}H_{30}N_2O_9$ requires C 54.3, H 6.8, N 6.3%. From a similar series of co-crystallization using aqueous methanol (1:1 v/v) as a solvent, (1)–(3) were obtained. Analyses: (1) found C 55.1, H 8.0, N 9.9%; $C_{13}H_{20}N_2O_5$ requires C 54.9, H 7.1, N 9.9%; (2) found C 46.5, H 7.1, N 6.0%; $C_{18}H_{30}N_2O_{12}$ requires C 46.4, H 6.5, N 6.0%; (3) found C 47.7, H 5.8, N 7.0%; $C_{16}H_{24}N_2O_{10}$ requires C 47.5, H 6.0, N 6.9%. Crystals of (1)–(3) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. Data collection, structure solution and refinement

Diffraction data for (1), (2) and (3) were collected at 100 (2) K on a Nonius Kappa-CCD diffractometer, using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed (Ferguson, 1999; Gabe et al., 1989; Johnson, 1976; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997a,b; Spek, 2000).

For (1) and (3), the space group $P2_1/c$ was uniquely assigned from the systematic absences. Compound (2) is triclinic: the space group $P\bar{1}$ was assumed and confirmed by the structure analysis. The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based upon

Figure 1
The molecular components of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
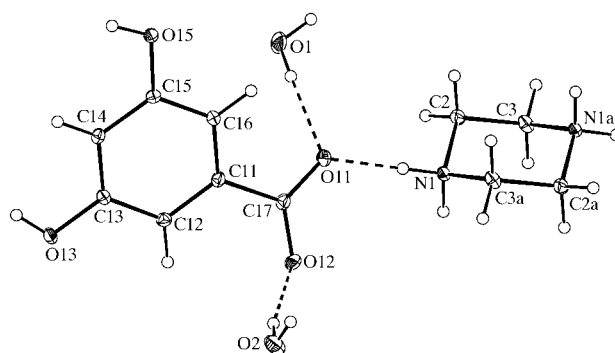
Figure 2
The molecular components of (2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 1
Experimental details.

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_6H_{13}N_2 \cdot C_7H_5O_4 \cdot H_2O$	$C_4H_{12}N_2 \cdot 2(C_7H_5O_4) \cdot 4(H_2O)$	$C_2H_{10}N_2 \cdot 2(C_7H_5O_4) \cdot 2(H_2O)$
Chemical formula weight	284.31	466.44	404.37
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, b, c (Å)	9.4478 (4), 11.7644 (4), 25.9024 (12)	7.7793 (3), 8.1656 (3), 9.0662 (4)	8.0804 (3), 10.6021 (6), 11.3988 (6)
α, β, γ (°)	90, 101.969 (2), 90	104.981 (2), 97.134 (2), 98.066 (2)	90, 109.243 (3), 90
V (Å^3)	2816.4 (2)	543.02 (4)	921.97 (8)
Z	8	1	2
D_x (Mg m^{-3})	1.341	1.426	1.457
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	15 105	5313	2104
θ range (°)	2.79–27.47	2.62–27.41	2.67–27.45
μ (mm^{-1})	0.103	0.121	0.122
Temperature (K)	100 (2)	100 (2)	100 (2)
Crystal form, colour	Plate, colourless	Block, colourless	Block, colourless
Crystal size (mm)	$0.30 \times 0.25 \times 0.13$	$0.36 \times 0.35 \times 0.25$	$0.20 \times 0.20 \times 0.13$
Data collection			
Diffractometer	Kappa-CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.9697	0.9579	0.9760
T_{max}	0.9867	0.9705	0.9843
No. of measured, independent and observed parameters	15 105, 6382, 3976	5313, 2430, 2133	21 623, 2104, 1756
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.028	0.022	0.024
θ_{max} (°)	27.47	27.41	27.45
Range of h, k, l	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 10$	$0 \rightarrow h \rightarrow 10$
	$-15 \rightarrow k \rightarrow 0$	$-10 \rightarrow k \rightarrow 10$	$0 \rightarrow k \rightarrow 13$
	$-33 \rightarrow l \rightarrow 32$	$-11 \rightarrow l \rightarrow 11$	$-14 \rightarrow l \rightarrow 13$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0538, 0.1313, 1.045	0.037, 0.0957, 1.055	0.041, 0.1125, 1.056
No. of reflections and parameters used in refinement	6382, 379	2430, 169	2104, 146
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.0968P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.2285P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.3193P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.000	0.015
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.281, −0.224	0.371, −0.24	0.262, −0.246
Extinction method	None	None	*SHELXL* (Sheldrick, 1997*b*)
Extinction coefficient	–	–	0.021 (6)

Computer programs used: *Kappa-CCD Server Software* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL* (Sheldrick, 1997*b*), *Word Perfect* macro PRPKAPPA (Ferguson, 1999), *NRCVAX*96 (Sheldrick, 1997*b*).

$P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). All H atoms were located from difference maps and all were included in the refinements as riding atoms with O−H (phenolic) 0.84, N−H 0.91–0.93, C−H 0.95 (aromatic) and 0.99 Å (CH$_2$): the O−H distances and H−O−H angles in water molecules were refined subject to soft constraints using *DFIX* commands (Sheldrick, 1997*a*). It was apparent at an early stage in the refinements that one H atom had been transferred from each acid unit to the diamine units. In (3) the unique water molecule in the asymmetric unit is

disordered over three sites. Initially, the site-occupation factors (s.o.f.s) were refined independently, but as these summed to unity, the s.o.f.s were subsequently constrained to sum to unity. There is a major site, with s.o.f 0.874 (6), and for this site the H atoms were located. For the two minor sites, with s.o.f.s 0.075 (6) and 0.052 (3), the H atoms could not be located.

The diagrams were prepared with the aid of *PLATON* (Spek, 2000). Hydrogen-bond dimensions are presented in Table 2 and other selected dimensions in Table 3.[1] Figs. 1–3 show the molecular components, with the atom-labelling schemes. Figs. 4–14 illustrate aspects of the supramolecular structures.

3. Results and discussion

3.1. Co-crystallization behaviour and molecular constitutions

From solutions in anhydrous methanol as the solvent, 3,5-dihydroxybenzene and the amines (II)–(V) all co-crystallize to give anhydrous products, (4)–(7), respectively, having amine-to-acid ratios of 1:2. In this respect, they closely resemble the adducts formed between 3,5-dinitrobenzoic acid and the same amines, all of which are salts containing doubly protonated amines and pairs of 3,5-dinitrobenzoate anions (Burchell *et al.*, 2001). Accordingly, it is reasonable to assume similar molecular constitutions for (4)–(7), although the supramolecular structures will be significantly different, consequent upon the change from weak hydrogen-bond acceptor nitro groups in 3,5-dinitrobenzoic acid to strong hydrogen-bond donor and acceptor groups in 3,5-dihydroxybenzoic acid. While the 3,5-dinitrobenzoate salts all crystallized very readily to give excellent crystals, none of (4)–(7) has

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0115). Services for accessing these data are described at the back of the journal.

Table 2
Hydrogen-bond dimensions (Å, °).

Compound (1)			
O1—H1A···O22[i]	1.85	2.743 (2)	167
O1—H1B···O11[ii]	1.92	2.834 (2)	173
O2—H2B···O11	1.96	2.827 (2)	163
O15—H15···O1	1.82	2.656 (2)	175
O23—H23···O12[iii]	1.85	2.684 (2)	175
O25—H25···O2	1.81	2.649 (2)	175
O2—H2A···N42[iv]	1.89	2.822 (2)	173
O13—H13···N32[i]	1.93	2.750 (2)	167
N31—H31···O11	1.84	2.750 (2)	165
N41—H41···O22	1.65	2.575 (2)	173
Compound (2)			
O1—H1A···O2[v]	1.85 (2)	2.694 (2)	176 (2)
O1—H1B···O11	1.99 (2)	2.834 (2)	176 (2)
O2—H2A···O11[vi]	2.02 (2)	2.856 (2)	175 (2)
O2—H2B···O12	1.94 (2)	2.759 (2)	163 (2)
O13—H13···O1[vii]	1.78	2.618 (2)	176
O15—H15···O12[viii]	1.79	2.627 (2)	172
N1—H1C···O13[ix]	2.05	2.858 (2)	145
N1—H1D···O11	1.80	2.718 (2)	178
Compound (3)			
O3—H3···O1[x]	1.78	2.622 (2)	175
O5—H5···O11[xi]	1.79	2.625 (3)	172
O11—H111···O3	2.13	2.950 (2)	168
O11—H112···O2[xii]	1.88	2.713 (3)	171
N1—H1A···O5[xiii]	2.03	2.839 (2)	147
N1—H1B···O2	1.83	2.729 (2)	169
N1—H1C···O1[iv]	1.89	2.778 (2)	166

Symmetry codes: (i) $x, \frac{1}{2} - y, -0.5 + z$; (ii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, 1 + y, z$; (iv) $x, \frac{3}{2} - y, -\frac{1}{2} + z$; (v) $x, y, 1 + z$; (vi) $1 - x, -y, -z$; (vii) $-x, -1 - y, -z$; (viii) $x, -1 + y, z$; (ix) $-x, -y, -z$; (x) $-1 + x, y, z$; (xi) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (xii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (xiii) $1 - x, 1 - y, 2 - z$.

so far been found to provide crystals suitable for single-crystal X-ray diffraction.

A second difference between these two series of salts is the ready propensity of the 3,5-dihydroxybenzoates to form hydrates: diamine (VI) forms a hydrate (8) with 3,5-dihydroxybenzoic acid, even from solutions in anhydrous methanol, presumably by absorption of atmospheric moisture during crystallization. When the solvent for co-crystallization
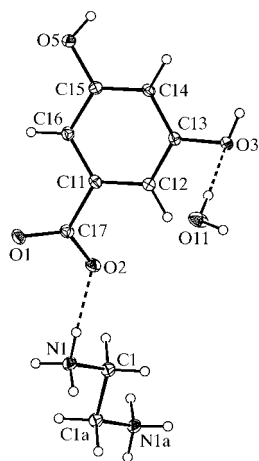
was changed from anhydrous methanol to aqueous methanol for amines (II), (III) and (V), in an attempt to grow crystals of better quality, the resulting crystalline products (1)–(3) were all hydrated to different degrees. These compounds contain one, four and two molecules, respectively, of water per molecule of amine, and in addition the amine-to-acid ratio in (1) is 1:1, rather than the 1:2 observed in all of the analogous systems. Since with aliphatic amines, 3,5-dihydroxybenzoic acid transfers to the amine the carboxyl proton, but neither of the phenolic protons, the diamine in (1) is only singly proto-nated, rather than doubly protonated, as in (2) and (3), and as in analogous 3,5-dinitrobenzoates (Burchell *et al.*, 2001).

It is notable that in none of the adducts (1)–(8) reported here is there any evidence for the incorporation of methanol, as opposed to water, in the hydrogen-bonded structures. Such incorporation is in fact rather common in salt-type adducts formed between aliphatic amines and phenolic hydrogen-bond donors (Ferguson *et al.*, 1998: Glidewell, Ferguson, Gregson & Campana, 2000; Gregson *et al.*, 2000).

3.2. Supramolecular structures

3.2.1. Compound (1). The constitution of (1) is that of a hydrated salt [HN(CH₂CH₂)₃N]⁺·[(HO)₂C₆H₃COO]⁻·H₂O: a single proton has been transferred from the acid to the diamine, which is thus only mono-protonated. This salt crys-tallizes in $P2_1/c$ with $Z' = 2$, so that the asymmetric unit contains two cations, two anions and two water molecules: the correctness of the $Z' = 2$ assignment is confirmed both by the
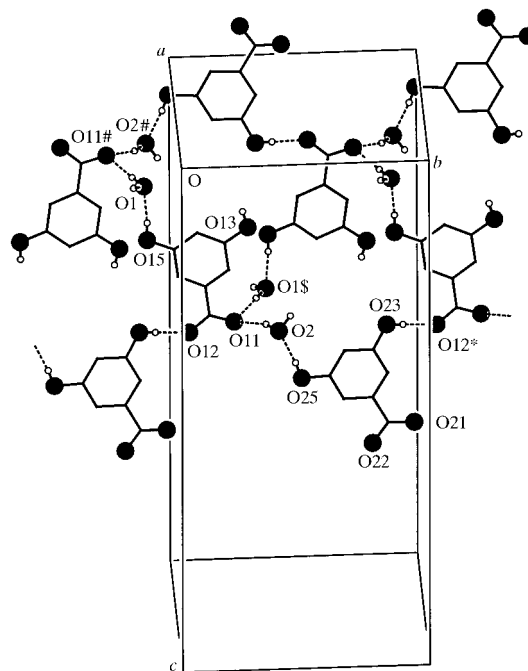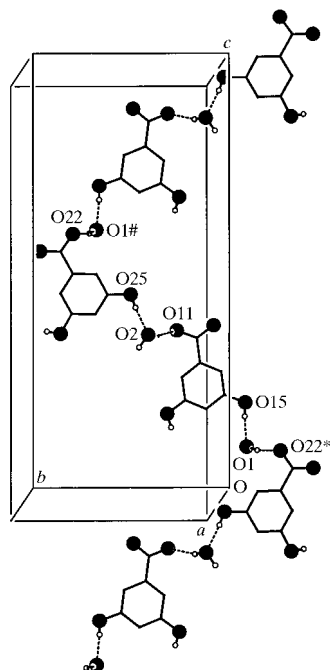

Figure 3
The molecular components of (3), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Figure 4
Part of the crystal structure of (1) showing the formation of a double chain of anions and water molecules parallel to [010]. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*), hash (#) or dollar ($) sign are at the symmetry positions $(x, 1 + y, z)$, $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

Table 3
Selected molecular dimensions (Å, °).

Compound (1)

N31—C31	1.498 (2)	N41—C41	1.486 (2)
N31—C33	1.495 (2)	N41—C43	1.493 (2)
N31—C35	1.497 (2)	N41—C45	1.491 (2)
N32—C32	1.469 (2)	N42—C42	1.475 (2)
N32—C34	1.470 (2)	N42—C44	1.480 (2)
N32—C36	1.466 (3)	N42—C46	1.477 (2)
N31—C31—C32—N32	0.6 (2)	N41—C41—C42—N42	−9.7 (2)
N31—C33—C34—N32	2.5 (2)	N41—C43—C44—N42	−8.2 (2)
N31—C35—C36—N32	2.4 (2)	N41—C45—C46—N42	−7.6 (2)
C12—C11—C17—O11	−14.1 (3)	C22—C21—C27—O21	7.5 (3)

Compound (2)

N1—C2	1.493 (2)	N1—C3^i	1.494 (2)
C12—C11—C17—O11	154.5 (1)	C12—C11—C17—O12	−24.9 (2)

Compound (3)

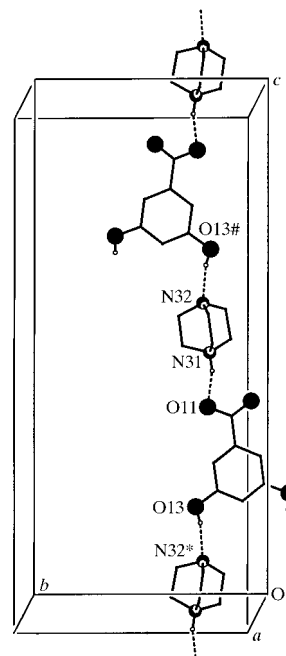|			
N1—C1	1.485 (1)		
C12—C11—C17—O1	143.9 (1)	C12—C11—C17—O2	−35.3 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

different conformations of the two independent anions (Fig. 1) and, more generally, by the different hydrogen-bonding characteristics of the chemically equivalent components (Table 2). Thus, for example, the water molecule containing O1 acts as a hydrogen-bond donor in two O—H···O hydrogen bonds, while that containing O2 is a donor in one O—H···O hydrogen bond and in one O—H···N hydrogen bond. Similarly the hydroxyl O atoms in the two anions exhibit different

patterns of behaviour: O13 and O15 are donors to N and O, respectively, while O23 and O25 are both donors to O. Finally, the two unprotonated N atoms both act as acceptors in O—H···N hydrogen bonds, N32 from phenolic O13 and N42 from water O2 (Table 2).

In hydrogen-bonded systems such as (1), the choice of asymmetric unit is arbitrary in terms of the relative disposition of the independent molecular components. It is not possible to select an unbranched asymmetric unit for (1) and the asymmetric unit (Fig. 1) has been selected so that it contains two cation–anion–water sequences, with a branching point at O11, near the middle of the overall unit. There are ten independent hard (Braga *et al.*, 1995) hydrogen bonds in the structure, six of O—H···O type and two each of types O—H···N and N—H···O. Of these, three of the O—H···O and both the N—H···O hydrogen bonds serve to link together the independent components within the selected asymmetric unit. In addition to these five intra-unit hydrogen bonds, there are five inter-unit hydrogen bonds, three of O—H···O type and two of O—H···N type.

For the description of complex supramolecular systems such as this, two complementary approaches, based respectively on the identification of a supermolecule and on the identification of sub-structures, have been found to be valuable (Glidewell, Ferguson, Gregson & Campana, 2000; Gregson *et al.*, 2000). In (1) the substructure approach provides the simpler description: the anions and the water molecules are linked by O—H···O hydrogen bonds to form sheets parallel to (100), which are further reinforced by the cations.

Figure 5
Part of the crystal structure of (1) showing the formation of a $C_4^4(18)$ anion–water chain parallel to [001]. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively.

Figure 6
Part of the crystal structure of (1), showing the formation of a $C_2^2(12)$ cation–anion chain parallel to [001]. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively.

As a sub-set of the asymmetric unit (Fig. 1) the anions and the water molecules form an unbranched tetramolecular aggregate. These units are linked into sheets whose formation is most easily described in terms of two one-dimensional motifs, forming chains running parallel to [001] and [010], respectively.

Atom O1, at (x, y, z), acts as a donor, via H1B, to O11 at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, while O1 at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ in turn acts as a donor to O11 at $(x, -1 + y, z)$, generating a spiral $C_2^2(9)$ chain around the 2_1 axis along $(\frac{1}{2}, y, \frac{1}{4})$. At the same time hydroxyl O23 at (x, y, z) acts as a donor to the carboxylic O12 at $(x, 1 + y, z)$, thus producing by translation a $C_3^3(12)$ chain. The $C_2^2(9)$ and $C_3^3(12)$ chains both run parallel to [010] and together they generate a double chain built from a single type of $R_7^6(28)$ ring (Fig. 4). Two such chains run through each unit cell. At the same time, O1 at (x, y, z) acts as a donor, via H1A to O22 at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$, while O1 at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ in turn acts as a donor to O22 at $(x, y, -1 + z)$, thus producing a zigzag $C_4^4(18)$ chain running parallel to [001] and generated by the action of the glide plane at $y = \frac{1}{4}$ (Fig. 5): again, two of these chains run through each unit cell.

The combination of the [001] and [010] chains gives rise to anion–water sheets parallel to (100) in which the hydrogen bonding is of some complexity. Each of the four molecule aggregates containing two anions and two water molecules is linked by inter-unit O—H···O hydrogen bonds to six other such aggregates. The hydrogen-bonding complexity is further

increased by the presence of the cations, whose incorporation does not, however, increase the dimensionality of the supramolecular structure, because each cation is linked to a single anion/water sheet by means of one O—H···N hydrogen bond and one N—H···O hydrogen bond.

Hydroxyl O13 at (x, y, z) acts as a donor to N32 at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$, while O13 at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ in turn acts as a donor to N32 at $(x, y, -1 + z)$, thus producing a $C_2^2(12)$ chain parallel to [001] generated by the glide plane at $y = \frac{1}{4}$ (Fig. 6). At the same time, water O2 at (x, y, z) acts as a donor, via H2A to N42 at $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$, thus producing a $C_3^3(14)$ chain, also parallel to [001] but generated by the glide plane at $y = \frac{3}{4}$ (Fig. 7). The (100) sheet thus utilizes the entire contents, neutral and ionic, of the unit cell and hence one such sheet is sufficient to completely describe the supramolecular structure.

3.2.2. Compound (2). The constitution of (2) is that of a hydrated salt $[H_2N(CH_2CH_2)_2NH_2]^{2+} \cdot 2[(HO)_2C_6H_3 \cdot COO]^- \cdot 4H_2O$, in which each molecule of the acid has transferred one proton to the piperazine. The cation lies across a centre of inversion, chosen for the sake of convenience as that at the cell centre, while the anion and the water molecules all lie in general positions. An extensive network of hydrogen bonds links the individual molecular components into a single three-dimensional framework. The two independent water molecules and the anion all act as double donors in O—H···O hydrogen bonds: each of O1 and O2 acts as a single acceptor and the carboxylate atoms O11 and O12 both act as double acceptors in O—H···O hydrogen bonds. By contrast, neither of the hydroxyl O atoms in the anion, O13 and O15, acts as an acceptor, although both act as donors.
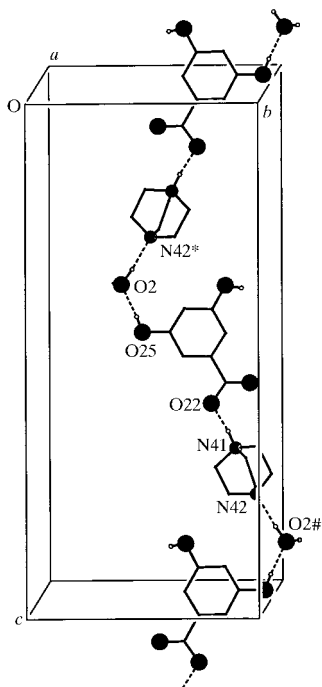

Figure 7
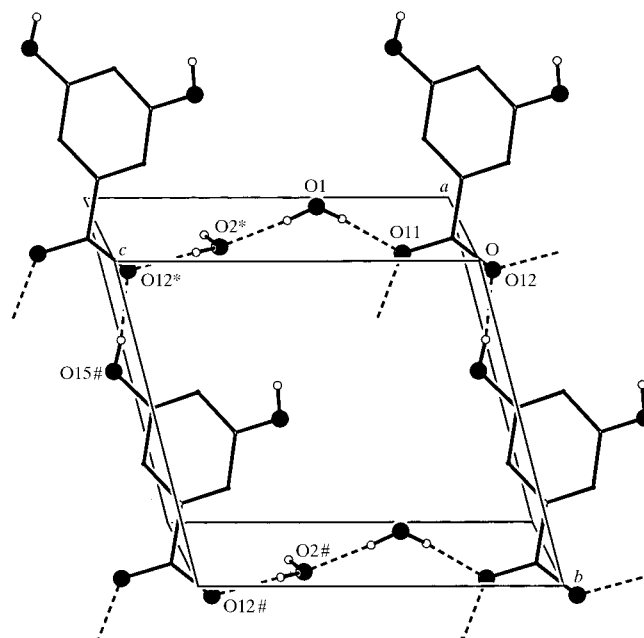Part of the crystal structure of (1), showing the formation of a three-component $C_3^3(14)$ chain parallel to [001]. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(x, \frac{3}{2} - y, \frac{1}{2} + z)$, respectively.

Figure 8
Part of the crystal structure of (2) showing the the formation of a (100) sheet of anions built from $R_8^8(28)$ rings. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(x, y, 1 + z)$ and $(x, 1 + y, 1 + z)$, respectively.

Adopting the substructure approach to the analysis of multi-dimensional supramolecular structures (Gregson *et al.*, 2000), it is possible to identify a continuous three-dimensional framework built from anions and water molecules only. This framework encapsulates large voids which contain the centrosymmetric cations. Each cation is linked to the oxygen-based framework by means of four N—H···O hydrogen bonds: the two distinct types of N—H···O hydrogen bonds utilize O11 and O13 as the acceptors. Hence, O11 is overall a triple acceptor of hydrogen bonds, O12 is a double acceptor, and O1, O2 and O13 are single acceptors: O15 does not accept any kind of hydrogen bond. The construction of the anion–water framework can be considered in many ways, but it is most simply and most elegantly analysed in terms of intersecting sheets parallel to (100) and ($\bar{1}$10), of which the (100) sheet is itself readily analysed in terms of individual one-dimensional motifs parallel to [010] and [001], respectively.

Hydroxyl O15 in the anion at (x, y, z) acts as a donor to carboxylate O12 in the anion at $(x, -1 + y, z)$, thus producing by translation a $C(7)$ chain parallel to [010] (Fig. 8). The [001] chains by contrast involve water molecules as well as anions. Within the asymmetric unit O1 is a donor, *via* H1*B*, to carboxylate O11, and O2 is a donor, *via* H2*B* to carboxylate O12 (Fig. 2): in addition, O1 at (x, y, z) acts as a donor, *via* H1*A*, to O2 at $(x, y, 1 + z)$, thus producing, again by translation, a $C_3^3(8)$ chain parallel to [001] (Fig. 8). The combination of these [010] and [001] chains generates a continuous sheet parallel to (100) and built from a single type of $R_8^8(28)$: two such sheets related to one another by the centres of inversion pass through each unit cell, one in the domain $-0.09 < x < 0.45$ and the other in the domain $0.62 < x < 1.09$.

The ($\bar{1}$10) sheet, on the other hand, is built from four different types of ring (Fig. 9). The $C_3^3(8)$ chain parallel to [001], described above, can also be identified in the ($\bar{1}$10) sheet, and symmetry-related chains of this type are linked into sheets by further hydrogen bonds in which atoms O2 and O13
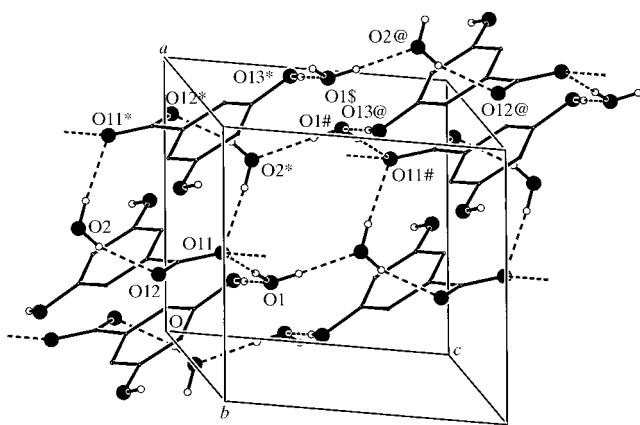
are the donors. Water O2 at (x, y, z) is a donor *via* H2*A* to carboxylate O11 at $(1 - x, -y, -z)$, while hydroxyl O13 at (x, y, z) is a donor to water O1 at $(-x, -1 - y, -z)$. Propagation of these interactions generates the ($\bar{1}$10) sheet (Fig. 9), in which there are $R_4^4(12)$, $R_4^4(18)$, $R_6^4(12)$ and $R_6^6(22)$ rings centred at $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$, respectively.

Combination of these two sheets generates a three-dimensional framework. This framework alone would encapsulate large voids at the centre of each unit cell (Fig. 10), amounting to *ca* 24% of the overall cell volume. In the event, these potential voids are occupied by the centrosymmetric cations. Each cation is linked by N—H···O hydrogen bonds to four different $C_3^3(8)$ chains of anions and water molecules (Fig. 11). N1 at (x, y, z) is linked, *via* H1*D* and H1*C*, to O11 at (x, y, z) and to O13 at $(-x, -y, -z)$, respectively, which are components of the $C_3^3(8)$ chains lying approximately along $(0.3, 0, z)$ and $(-0.3, 0, z)$. Similarly, the symmetry-related N1 in the same cation, which is at $(1 - x, 1 - y, 1 - z)$ forms N—H···O hydrogen bonds to O11 and O13 at $(1 - x, 1 - y, 1 - z)$ and $(1 + x, 1 + y, 1 + z)$, respectively, components of the $C_3^3(8)$ chains lying approximately along $(0.7, 1.0, z)$ and $(1.3, 1.0, z)$, respectively (Fig. 11).

3.2.3. Compound (3). Compound (3) is a salt $[H_3NCH_2CH_2NH_3]^{2+}\cdot2[(HO)_2C_6H_3COO]^-\cdot2H_2O$ (Fig. 3) and its overall constitution is closely similar to that of (2) (see §3.2.2). The cation lies across a centre of inversion chosen, as for (2), as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The three-dimensional framework which results from the hydrogen bonding can most simply be described in terms of a series of two-component, one-dimensional motifs running parallel to the [100], [010] and [001] directions, respectively.

The anions form $C(7)$ chains along [100]: hydroxyl O3 at (x, y, z) acts as a donor to carboxylate O1 at $(-1 + x, y, z)$ (Fig. 12). Four such chains run through each unit cell and antiparallel pairs of chains are linked into molecular ladders by the centrosymmetric cations: N1 at (x, y, z) acts as a donor, *via* H1*B*, to O2 within the asymmetric unit. Propagation of these two interactions then generates the ladder along [100], in which the $C(7)$ chains form the uprights and the cations form the rungs: between the rungs there are centrosymmetric $R_6^6(32)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer; Fig. 12).

Figure 9
Part of the crystal structure of (2) showing the formation of a ($\bar{1}$10) sheet built from four different types of ring. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*), hash (#), dollar ($) or at (@) sign are at the symmetry positions $(1 - x, -y, -z)$, $(1 - x, -y, 1 - z)$, $(1 + x, 1 + y, z)$ and $(1 + x, 1 + y, 1 + z)$, respectively.
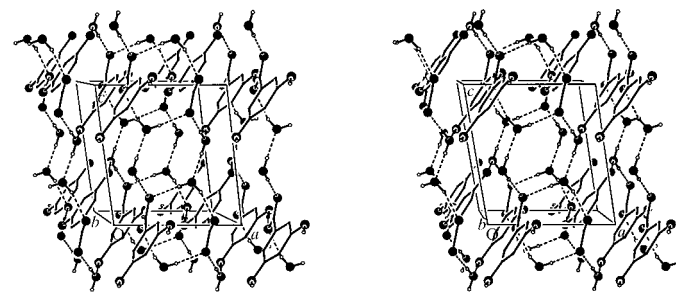

Figure 10
Stereoview of part of the crystal structure of (2), showing one of the voids within the three-dimensional anion–water framework. For the sake of clarity, H atoms bonded to C are omitted.

The water molecules do not participate in the formation of the [100] ladders, but by acting as double donors in O—H$\cdots$O hydrogen bonds, they link the anions into spiral chains running parallel to the [010] direction. The water O11 atom acts as a donor, *via* H111, to hydroxyl O3 within the asymmetric unit: in addition, O11 at (x, y, z) also acts as a donor, *via* H112, to carboxylate O2 at $(-x, \frac{1}{2}+y, \frac{3}{2}-z)$: O11 at $(-x, \frac{1}{2}+y, \frac{3}{2}-z)$ in turn acts as a donor to O2 at $(x, 1+y, z)$, thus producing a $C_2^2(9)$ chain running parallel to [010] (Fig. 13) and generated by the 2_1 screw axis along $(0, y, \frac{3}{4})$. Two of these anion/water spirals pass through each unit cell and they reinforce the linking of the [100] ladders into a two-dimensional array.

The [001] motif takes the form of a chain of rings (Fig. 14). As well as acting as a donor to O2 within the asymmetric unit, N1 at (x, y, z) also acts as a donor to O5 at $(1-x, 1-y, 2-z)$ thus forming an $R_4^4(18)$ motif. Propagation of these two interactions *via* the centrosymmetric cation leads to the formation of a $C_2^2(12)$ [$R_4^4(18)$] chain of rings along which the $R_4^4(18)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, n)$ alternate with cations centred at $(\frac{1}{2}, \frac{1}{2}, n + \frac{1}{2}$; n = zero or integer).

These three motifs (Figs 12–14) link all the components within the unit cell into a single three-dimensional framework, the formation of which by these means does not, however, utilize all the hydrogen-bonding capacity in the structure. Two additional motifs reinforce the framework. The [100] ladder described above lies in the domain $0.28 < y < 0.72$ and a second ladder, related to the first by the action of the translational
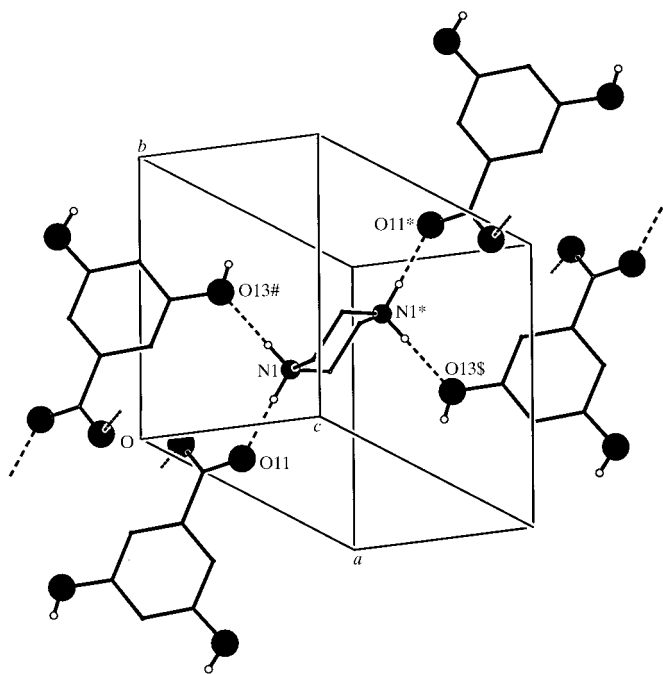
symmetry operators, lies in the domain $0.78 < y < 1.22$. The formation of each ladder utilizes only one hydroxyl group per anion and only two of the six N—H bonds per cation and a further type of N—H$\cdots$O hydrogen bond links neighbouring ladders. Atom N1 at (x, y, z), a component of a ladder in the domain $0.28 < y < 0.72$, acts as a donor, *via* H1C, to O1 at $(x, \frac{3}{2}-y, -\frac{1}{2}+z)$, a component of a ladder in the domain $0.78 < y < 1.22$. The symmetry-related N1 in the same cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is at $(1-x, 1-y, 1-z)$ and this atom acts as a donor to O1 at $(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, a component of a ladder in the domain $-0.22 < y < 0.22$. Hence, this type of N—H$\cdots$O hydrogen bond links each ladder to two neighbouring ladders. Similarly, adjacent [010] spirals are linked by a further type of O—H$\cdots$O hydrogen bond. Hydroxyl O5 at (x, y, z) is a component of the spiral along $(0, y, \frac{3}{4})$ (Fig. 13), and it acts as a donor to water O11 at $(x, \frac{3}{2}-y, \frac{1}{2}+z)$, a component of the anion/water spiral along $(0, y, 1.25)$. The symmetry-related O5 in the $(0, y, \frac{3}{4})$ spiral is at $(-x, \frac{1}{2}+y, \frac{3}{2}-z)$ and thus acts as a donor to O11 at $(-x, 2-y, 1-z)$, which is a component of the anion/water spiral along $(0, y, \frac{1}{4})$. Hence, each [010] spiral is linked to the two adjacent spirals along the [001] direction in a $C_2^2(9)$ motif.

Of the three one-dimensional motifs in (3) two, those along the [100] and [010] directions, are each built from just two of the individual components. The [100] ladders are built from cations and anions only, while the [010] chains are built from anions and water molecule only. However, there is no motif in (3) built from the other pairwise combination of building blocks, cations and water molecules, as there are no direct
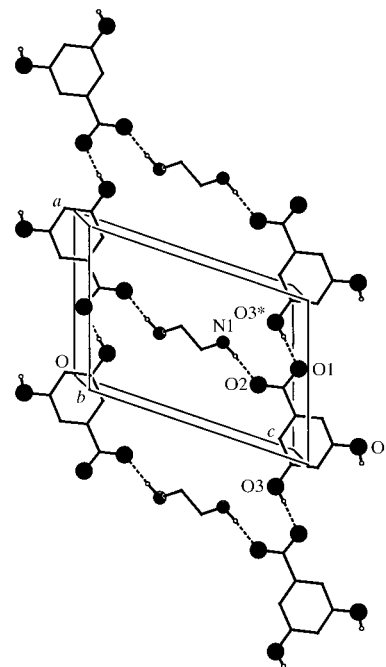

Figure 11
Part of the crystal structure of (2) showing the linking of a centrosymmetric cation to four different anions, each a component of a different [001] chain. For the sake of clarity, H atoms bonded to C are omitted. Atoms marked with a star (*), hash (#) or dollar ($) sign are at the symmetry positions $(1-x, 1-y, 1-z)$, $(-x, -y, -z)$ and $(1+x, 1+y, 1+z)$, respectively.

Figure 12
Part of the crystal structure of (3) showing the formation of a molecular ladder parallel to [100]. For the sake of clarity, H atoms bonded to C or N and not participating in the hydrogen-bonding motif shown are omitted. The atom marked with a star (*) is at the symmetry position $(1+x, y, z)$.

hydrogen bonds between these components. The cation is a donor only to O acceptors in anions, while the water molecule is a donor to, and acceptor from, anions only (Table 2). It is thus not possible to identify here a hierarchy of N-dimensional, N-component substructures, as is sometimes found (Glidewell, Ferguson & Lough, 2000).

3.3. Hydrogen-bond dimensions

The dimensions of the hydrogen bonds (Table 2) require only brief comment. The N—H···O hydrogen bonds can be divided into two categories, both of which involve cationic N: the O acceptor can be anionic (carboxylate) or neutral (phenolic or water). For anionic O, when both donor and acceptor are thus charged, the ranges of the H···O and N···O distances are 1.65–1.89 and 2.575 (2)–2.778 (2) Å, respectively, with a mean N—H···O angle of 170°. The two examples with neutral O acceptors both have H···O (range 2.03–2.05 Å) and N···O [range 2.839 (2)–2.858 (2) Å] longer than any of those with an anionic acceptor, as usually found (Aakeröy & Seddon, 1993; Gilli et al., 1994) and their N—H···O angles are correspondingly much smaller, 145 and 147°.

The O—H···O hydrogen bonds can similarly be divided into two groups according to whether the acceptor is anionic or neutral. In the first group there are nine examples: the O···O distances span the range 2.622 (2)–2.856 (2) Å with a mean value of 2.763 Å, and the closely grouped O—H···O angles have a mean value of 171°. It might be expected that those O—H···O hydrogen bonds with neutral acceptors would, in general, be longer and weaker than those with

anionic acceptors. Although this is so for the single example, in (3), having a phenolic acceptor, where H···O is 2.13 Å and O···O is 2.950 (2) Å, all those with water O as an acceptor have very short H···O distances in the range 1.78–1.85 Å and very short O···O distances in the range 2.618 (2)–2.694 (2) Å, with mean value 2.648 (2) Å.

3.4. Molecular conformations and dimensions

In (1), the C—N distances in the cations (Table 3) exhibit a clear distinction between those involving protonated N and those involving neutral N; the mean values for the two types are 1.494 (2) and 1.473 (3) Å, with no overlapping of their ranges. The C—N distances in the cations of (2) and (3), where all the N are protonated, are all, within experimental uncertainty, within the range of the longer type in (1). The other bond distances are all typical of their types (Allen et al., 1987) and present no unusual features. The bond angles at the C atoms ipso to the phenolic OH group in all compounds exhibit the usual pattern of behaviour with the O—C—C angles syn to H much larger than those anti to H. The carboxylate O—C—O angles are all significantly greater than 120°.

The twist of the cation skeletons in (1) away from idealized D_{3h} symmetry towards D_3 generally observed in salts and adducts is markedly different in the two independent cations. The mean values of the N—C—C—N torsional angles in the two cations are +1.8 (6) and −8.5 (6)°. There are also very striking differences between the conformations of the anions in (1)–(3), in terms of the degree of twist of the carboxylate
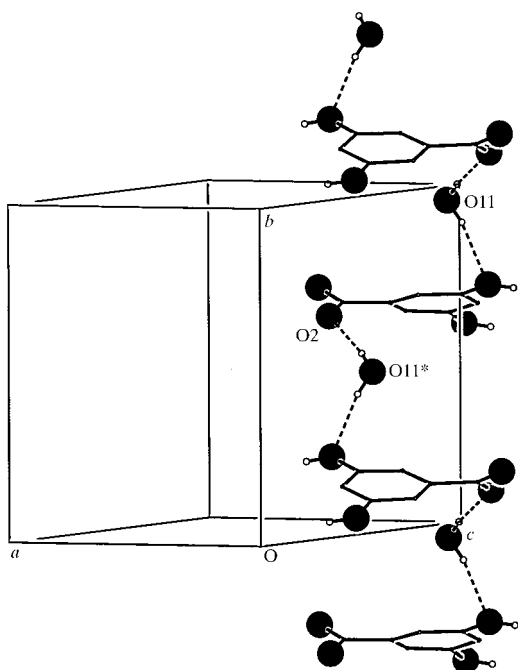

Figure 13
Part of the crystal structure of (3) showing the formation of a $C_2^2(9)$ spiral chain parallel to [010] along the 2_1 axis at $(0, y, \frac{3}{4})$. For the sake of clarity, H atoms bonded to C are omitted. The atom marked with a star (*) is at the symmetry position $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$.
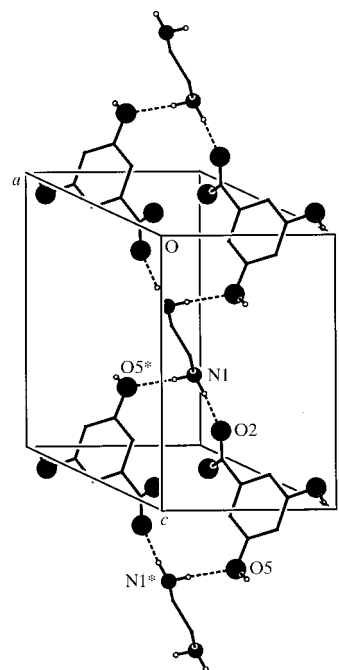

Figure 14
Part of the crystal structure of (3) showing the formation of a $C_2^2(12)$ $[R_4^4(18)]$ chain of rings parallel to [001] along the 2_1 axis at $(0, y, \frac{3}{4})$. For the sake of clarity, H atoms bonded to C or N and not participating in the hydrogen-bonding motif shown are omitted. The atoms marked with a star (*) are at the symmetry position $(1 - x, 1 - y, 2 - z)$.

group out of the plane of the adjacent aryl ring. This ranges from 7.5° in one of the anions in (1) to *ca* 35° in (3) (Table 3), but there is no clear pattern of correlation between the anion conformation and the local hydrogen-bonding arrangement.

4. Concluding comments

The structures reported here, and those reported earlier for other adducts of 3,5-dihydroxybenzoic acid with amines, demonstrate the remarkable structural versatility of this acid. In the single example so far recorded with a heteroaromatic amine, no proton transfer occurs (Wheatley *et al.*, 1999). With aliphatic amines, the 3,5-dihydroxybenzoate anion is always formed, but in the five salts investigated so far the degree of hydration differs widely. The anion alone can generate hydrogen-bonded sheets, as in the pillared-layer structure formed with the cation $[(tet-a)H_2]^{2+}$, or a three-dimensional framework, as with $[HN(CH_2CH_2NH_3)_2]^{2+}$. In combination with water molecules, the anion can form one-dimensional arrays as in (3), two-dimensional as in (1) or three-dimensional as in (2). The degree of hydration in salts and the consequent behaviour of the 3,5-dihydroxybenzoate cation are both unpredictable at the present time. When further empirical evidence becomes available, it may become possible to rationalize the behaviour of these systems into a predictive model.

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