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Two different three-dimensional hydrogen-bonded framework structures in two hydrated adducts *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–terephthalic acid–water (1/1/4) and (1/1/6)

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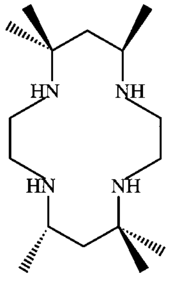
Co-crystallization of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $C_{16}H_{36}N_4$, with terephthalic acid (1,4-benzenedicarboxylic acid), $C_8H_6O_4$, from ethanol yields the tetrahydrate $(C_{16}H_{36}N_4).(C_8H_6O_4).(H_2O)_4$ (1), *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–terephthalic acid–water (1/1/4), while similar co-crystallization from methanol yields the hexahydrate $(C_{16}H_{36}N_4).(C_8H_6O_4).(H_2O)_6$ (2), *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–terephthalic acid–water (1/1/6). Both compounds are salts, $[C_{16}H_{38}N_4]^{2+}.[C_8H_4O_4]^{2-}.4H_2O$ (1) and $[C_{16}H_{38}N_4]^{2+}.[C_8H_4O_4]^{2-}.6H_2O$ (2): in (2) both ionic components lie across centres of inversion and in both salts there are two protons held within the N_4 cavity of the cation. In the structure of (1), the cations and anions are linked into chains by means of paired N—H···O hydrogen bonds, and the water molecules are linked into continuous chains by means of O—H···O hydrogen bonds, in which each of the H atoms is independently disordered over two equally populated sites. The water chains link the ionic chains into a continuous three-dimensional framework by means of further O—H···O hydrogen bonds. In (2) the cations and anions are linked by single N—H···O hydrogen bonds, again into chains: at the same time the anions and the water molecules are linked by multiple O—H···O hydrogen bonds into continuous two-dimensional nets, which are linked by the cations, by means of N—H···O hydrogen bonds into a three-dimensional framework, entirely different from that in (1).

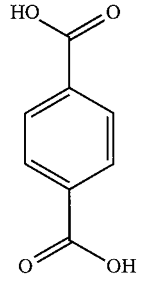
1. Introduction

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) (I), is a versatile molecular building block in supramolecular chemistry (Gregson *et al.*, 2000). This amine is strongly basic and readily captures two protons to form a dication $[C_{16}H_{38}N_4]^{2+}$ in which two H atoms are held in the interior N_4 cavity of the ring, forming a pair of intramolecular N—H···N hydrogen bonds. There are four external N—H bonds roughly normal to the ring and hence this dication could, in principle, act as a fourfold donor in hydrogen-bond formation in which the geometric arrangement of the hydrogen bonds is pre-determined.

Whereas the unmethylated analogue 1,4,8,11-tetraazacyclotetradecane, $C_{10}H_{24}N_4$ (cyclam), readily undergoes tetra-*N*-alkylation, tet-a undergoes only di-*N*-alkylation, at N1 and N8. The other two N sites, N4 and N11, appear to be protected by the adjacent gem-dimethyl substituents and the resulting dialkylated product from tet-a is centrosymmetric (Hay *et al.*, 1996). If this steric shielding of two of the N sites also applied to the hydrogen-bonding behaviour of the dication formed from tet-a, then this cation should provide a different hydrogen-bonding building block, with only two N—H bonds active as hydrogen-bond donors, one on each face of the macrocycle. In the salt-like adduct of tet-a with 3-hydroxybenzoic acid, it is indeed only the less sterically hindered axial N—H bonds which are active in hydrogen-bond formation, but in the corresponding adducts formed by both 4-hydroxybenzoic acid and 3,5-dihydroxybenzoic acid, all the axial N—H bonds are active (Gregson *et al.*, 2000). We have now extended this study to include the dicarboxylic acid terephthalic acid (benzene-1,4-dicarboxylic acid) (II), and here we report the structural analysis of two hydrated salts of stoichiometry tet-a–terephthalic acid–water (1/1/4) (1) and tet-a–terephthalic acid–water (1/1/6) (2). Both compounds are hydrated salts $[C_{16}H_{38}N_4]^{2+}.[C_8H_4O_4]^{2-}.4H_2O$ (1) and $[C_{16}H_{38}N_4]^{2+}.[C_8H_4O_4]^{2-}.6H_2O$ (2), but the supramolecular architectures are quite different. In particular, the cations and anions are linked into chains by paired N—H···O hydrogen bonds in (1) and by single N—H···O hydrogen bonds in (2), while the water molecules in these two compounds play entirely different roles. Furthermore, whereas the adducts of tet-a with 3-hydroxybenzoic acid, 4-hydroxybenzoic acid and 3,5-dihydroxybenzoic acid form structures which are respectively, one-, two- and three-dimensional (Gregson *et al.*, 2000), both the hydrated adducts with terephthalic acid (1) and (2) reported here form three-dimensional frameworks.



(I)



(II)

2. Experimental

2.1. Synthesis

Tet-a was prepared by the literature method (Hay *et al.*, 1975). Compounds (1) and (2) were prepared by co-crystallizing tet-a with terephthalic acid from solutions in ethanol and methanol, respectively: the two components were separately dissolved and these solutions were mixed and set aside to crystallize while exposed to the laboratory atmosphere. Analyses: (1) found: C 55.0, H 10.2, N 10.7%; $C_{24}H_{50}N_4O_8$ requires: C 55.2, H 9.6, N 10.7%; (2) found C 52.2, H 10.1, N 10.0%: $C_{24}H_{54}N_4O_{10}$ requires C 51.6, H 9.7, N 10.0%. Crystals 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) and (2) were collected at 100.0 (1) K using 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, 1997*a*,*b*; Spek, 1999). For (1) and (2) the space groups $P2_1/n$ and $P2_1/c$, respectively, were uniquely determined from the systematic absences. The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). No absorption corrections were necessary. All H atoms were located from difference maps and all were included in the refinements as riding atoms. It was apparent at an early stage in the refinements that two H atoms had been transferred from the acid units to the tet-a units. All H atoms are fully ordered, except for those in the water molecules of (1), where in each of the four independent water molecules, one of the H atoms (labelled H*n*1, for *n* = 3, 4, 5 or 6) is fully ordered, but the other is disordered over two sites: careful inspection of difference maps showed that the alternative sites were, for each molecule, equally populated, and hence the s.o.f.s of these disordered H atoms (labelled H*n*2 and H*n*3, for *n* = 3, 4, 5 or 6) were subsequently all fixed at 0.5. The distances O*n*—H*n*1 refined to a common value of 0.85 (1) Å; for H*n*2 and H*n*3, the O—H distances were all constrained to be 0.84 Å. The diagrams were prepared with the aid of *PLATON* (Spek, 1999). Hydrogen-bond dimensions are presented in Table 2 and other selected dimensions in Table 3.[1] Fig. 1 shows the asymmetric unit of (1), with the atom-labelling scheme, and Figs. 2–5 show aspects of the supramolecular structure; similarly for (2), Fig. 6 shows the molecular components and Figs. 7 and 8 show aspects of the molecular structure.

3. Results and discussion

3.1. Co-crystallization behaviour

The co-crystallization behaviour of tet-a with terephthalic acid is unusual and unexpected: the expected 1:1 salt is formed regardless of whether methanol or ethanol is used as the crystallization solvent, but the degree of hydration, and consequently the supramolecular architecture, appears to depend critically upon the solvent. When ethanol is used the salt is a tetrahydrate (1), but when methanol is the co-crystallization solvent a hexahydrate (2) is formed. In neither case is there any incorporation of the alcohol solvent into the structure and the water is presumably derived either from the atmosphere or from traces present in the organic solvents. In both compounds the stoichiometry is unambiguous and all the water molecules are intimately bound into the supramolecular

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0023). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$C_{16}H_{38}N_4.C_8H_4O_4.4H_2O$	$C_{16}H_{38}N_4.C_8H_4O_4.6H_2O$
Chemical formula weight	522.68	558.71
Cell setting	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	13.3213 (4)	8.1772 (3)
b (Å)	14.0499 (4)	12.3974 (4)
c (Å)	16.0491 (6)	16.8804 (5)
β (°)	110.549 (2)	116.231 (2)
V (Å^3)	2812.67 (16)	1535.04 (9)
Z	4	2
D_x (Mg m^{-3})	1.234	1.209
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	6427	3512
θ range (°)	4.08–27.48	4.10–27.48
μ (mm^{-1})	0.092	0.093
Temperature (K)	100.0 (1)	100.0 (1)
Crystal form	Block	Block
Crystal size (mm)	0.35 × 0.30 × 0.10	0.40 × 0.32 × 0.24
Crystal colour	Colourless	Colourless
Data collection		
Diffractometer	KappaCCD	KappaCCD
Data collection method	φ scans and ω scans with κ offsets	φ scans and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan
$T_{\min}$	0.9686	0.9638
$T_{\max}$	0.9909	0.9780
No. of measured reflections	32 836	16 757
No. of independent reflections	6427	3512
No. of observed reflections	4031	2756
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.082	0.040
$\theta_{\max}$ (°)	27.48	27.48
Range of h, k, l	$0 \rightarrow h \rightarrow 17$ $0 \rightarrow k \rightarrow 18$ $-20 \rightarrow l \rightarrow 19$	$0 \rightarrow h \rightarrow 10$ $-16 \rightarrow k \rightarrow 0$ $-21 \rightarrow l \rightarrow 18$
Refinement		
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0412	0.0380
$wR(F^2)$	0.0988	0.1077
S	0.914	0.978
No. of reflections used in refinement	6427	3512
No. of parameters used	371	195
H-atom treatment	Constrained	Constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 0.1606P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.002	0.000
$\Delta\rho_{\max}$ (e Å^{-3})	0.233	0.236
$\Delta\rho_{\min}$ (e Å^{-3})	−0.202	−0.261
Extinction method	*SHELXL* (Sheldrick, 1997*a*)	None
Extinction coefficient	0.0036 (7)	0
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1)
Computer programs		
Data collection	*KappaCCD* (Nonius, 1997)	*KappaCCD* (Nonius, 1997)
Cell refinement	*DENZO-SMN* (Otwinowski & Minor, 1997)	*DENZO-SMN* (Otwinowski & Minor, 1997)
Data reduction	*DENZO-SMN* (Otwinowski & Minor, 1997)	*DENZO-SMN* (Otwinowski & Minor, 1997)
Structure solution	*SHELXS*97 (Sheldrick, 1997*a*)	*SOLVER* in *NRCVAX*96 (Gabe *et al.*, 1989)
Structure refinement	*NRCVAX*96 (Gabe *et al.*, 1989) and *SHELXL*97 (Sheldrick, 1997*b*)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*)
Preparation of material for publication	*NRCVAX*96, *SHELXL*97 and *WordPerfect* macro PRPKAPPA (Ferguson, 1999)	*NRCVAX*96, *SHELXL*97 and *WordPerfect* macro PRPKAPPA (Ferguson, 1999)

structure, acting as both hydrogen-bond donors and hydrogen-bond acceptors. Since all the crystallographically distinct water molecules in both structures turn out to be acting as double donors of hydrogen bonds, the specificity of their incorporation, to the exclusion of any alcohol ROH capable of acting only as a single donor of hydrogen bonds, becomes intelligible. The crystallization of (1) and (2) as hydrates may also be contrasted with the behaviour of tet-a with the closely related acids 3- and 4-hydrodroxy benzoic acids: each of these aids forms a 1:2 salt with tet-a, $[C_{16}H_{38}N_4]^{2+}$.-$2[HOC_6H_4COO]^-$, but both are methanol solvates (Gregson *et al.*, 2000).

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

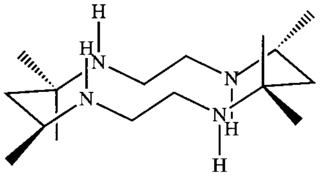
Compound (1)					
O3···O22	2.930 (2)	H31···O22	2.07	O3—H31···O22	174
O3···O4	2.797 (2)	H32···O4	1.97	O3—H32···O4	167
O3···O3$^{\rm i}$	2.908 (2)	H33···O3$^{\rm i}$	2.07	O3—H33···O3$^{\rm i}$	169
O4···O21$^{\rm ii}$	2.790 (2)	H41···O21$^{\rm ii}$	1.95	O4—H41···O21$^{\rm ii}$	169
O4···O5	2.855 (2)	H42···O5	2.03	O4—H42···O5	164
O4···O3	2.797 (2)	H43···O3	1.99	O4—H43···O3	160
O5···O23	2.821 (2)	H51···O23	1.98	O5—H51···O23	172
O5···O4	2.855 (2)	H52···O4	2.05	O5—H52···O4	159
O5···O6	2.805 (2)	H53···O6	1.96	O5—H53···O6	175
O6···O24$^{\rm iii}$	2.900 (2)	H61···O24$^{\rm iii}$	2.05	O6—H61···O24$^{\rm iii}$	175
O6···O6$^{\rm iv}$	2.781 (2)	H62···O6$^{\rm iv}$	1.95	O6—H62···O6$^{\rm iv}$	175
O6···O5	2.805 (2)	H63···O5	1.97	O6—H63···O5	168
N1···O24	2.714 (2)	H1*A*···O24	1.80	N1—H1*A*···O24	170
N4···O21$^{\rm v}$	2.997 (2)	H4*A*···O21$^{\rm v}$	2.11	N4—H4*A*···O21$^{\rm v}$	160
N8···O22$^{\rm v}$	2.720 (2)	H8*A*···O22$^{\rm v}$	1.80	N8—H8*A*···O22$^{\rm v}$	178
N11···O23	3.260 (2)	H11*A*···O23	2.48	N11—H11*A*···O23	142
N1···N11	2.852 (2)	H1*B*···N11	2.06	N1—H1*B*···N11	144
N8···N4	2.814 (2)	H8*B*···N4	2.04	N8—H8*B*···N4	141
Compound (2)					
O3···O11	2.749 (2)	H3*C*···O11	1.90 (2)	O3—H3*C*···O11	161
O3···O4	2.784 (2)	H3*D*···O4	1.91 (2)	O3—H3*D*···O4	172
O4···O5$^{\rm vi}$	2.769 (2)	H4*C*···O5$^{\rm vi}$	1.92 (2)	O4—H4*C*···O5$^{\rm vi}$	163
O4···O11$^{\rm vi}$	2.848 (2)	H4*D*···O11$^{\rm vi}$	1.98 (2)	O4—H4*D*···O11$^{\rm vi}$	169
O5···O12$^{\rm vii}$	2.784 (2)	H5*C*···O12$^{\rm vii}$	1.91 (2)	O5—H5*C*···O12$^{\rm vii}$	175
O5···O3	2.818 (2)	H5*D*···O3	1.95 (2)	O5—H5*D*···O3	171
N1···O12	2.719 (2)	H1*A*···O12	1.83	N1—H1*A*···O12	170
N4···O3$^{\rm viii}$	3.074 (2)	H4*A*···O3$^{\rm viii}$	2.20	N4—H4*A*···O3$^{\rm viii}$	163
N1···N4$^{\rm viii}$	2.818 (2)	H1*B*···N4$^{\rm viii}$	2.05	N1—H1*B*···N4$^{\rm viii}$	142

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

3.2. Supramolecular structures

In both (1) and (2) the cations $[C_{16}H_{38}N_4]^{2+}$ and the anions $[C_8H_4O_4]^{2-}$ are linked by means of N—H···O hydrogen bonds into one-dimensional chains: in the structures of both compounds, the complexity and the three-dimensionality are provided by the actions of the water molecules, whose dominant mode of association is chain formation in (1) and ring formation in (2).

3.2.1. Compound (1). All the components of the asymmetric unit (Fig. 1) lie in general positions, although both the ionic components are capable of lying across centres of inversion: indeed both ionic components in (2) do lie across inversion centres, as do the cations $[C_{16}H_{38}N_4]^{2+}$ in all previously reported adducts containing this cation (Gregson *et al.*, 2000). In (1) the cation, in fact, has a conformation close to the centrosymmetric *trans*-III type (Barefield *et al.*, 1986; Fig. 1 and Table 3), with four methyl groups in equatorial sites and two in axial sites (III), while the anion has a conformation close to $C_s(m)$ symmetry.



(III)

As expected, there are two additional protons within the N_4 cavity of the cations forming an $R_2^2(10)$ motif (Bernstein *et al.*, 1995). Within the asymmetric unit N1 and N11 act as hydrogen-bond donors to O24 and O23, respectively (Fig. 1), forming a further $R_2^2(10)$ ring, while the N—H bonds on the opposite face, at N4 and N8, form hydrogen bonds with O21 and O22, respectively, in the anion at $(-1 + x, y, z)$ in another, similar $R_2^2(10)$ ring. The ionic components thus form a chain-

Table 3
Selected geometric parameters (Å, °).

Compound (1)				Compound (2)	
N1—C14	1.507 (2)	N8—C7	1.506 (2)	N1—C7$^{\rm i}$	1.510 (2)
N1—C2	1.485 (2)	N8—C9	1.487 (2)	N1—C2	1.494 (2)
N4—C3	1.470 (2)	N11—C10	1.467 (2)	N4—C3	1.469 (2)
N4—C5	1.492 (2)	N11—C12	1.499 (2)	N4—C5	1.493 (2)
C27—O21	1.249 (2)	C28—O23	1.254 (2)	C14—O11	1.254 (2)
C27—O22	1.275 (2)	C28—O24	1.275 (2)	C14—O12	1.266 (2)
C14—N1—N2	113.8 (2)	C7—N8—C9	115.1 (2)	C7$^{\rm i}$—N1—C2	113.8 (2)
C3—N4—C5	115.2 (2)	C10—N11—C12	116.1 (2)	C3—N4—C5	115.9 (1)
O21—C27—O22	124.6 (2)	O23—C28—O24	124.2 (2)	O11—C14—O12	125.1 (2)
N1—C2—C3—N4	−65.4 (2)	N8—C9—C10—N11	63.9 (2)	N1—C2—C3—N4	−70.1 (2)
C2—C3—N4—C5	175.4 (2)	C9—C10—N11—C12	−168.0 (2)	C2—C3—N4—C5	169.2 (1)
C3—N4—C5—C6	170.3 (2)	C10—N11—C12—C13	−166.0 (2)	C3—N4—C5—C6	173.3 (1)
N4—C5—C6—C7	67.5 (2)	N11—C12—C13—C14	−73.3 (2)	N4—C5—C6—C7	71.7 (2)
C5—C6—C7—N8	−60.6 (2)	C12—C13—C14—N1	57.7 (2)	C5—C6—C7—N1$^{\rm i}$	−58.9(2)
C6—C7—N8—C9	161.5 (2)	C13—C14—N1—C2	−152.2 (2)	C6—C7—N1$^{\rm i}$—C2$^{\rm i}$	156.9 (1)
C7—N8—C9—C10	176.4 (2)	C14—N1—C2—C3	−177.7 (2)	C7—N1$^{\rm i}$—C2$^{\rm i}$—C3$^{\rm i}$	175.1 (1)
O21—C27—C21—C22	159.7 (2)	O24—C28—C24—C23	−161.2 (2)	O12—C14—C11—C12	160.6 (1)
O22—C27—C21—C22	−20.7 (2)	O23—C28—C24—C23	19.1 (2)	O11—C14—C11—C12	−20.1 (2)

† Symmetry code: (i) $1-x, 1-y, 1-z$.

of-rings, in which the $C_2^2(14)$ chain encompasses three distinct $R_2^2(10)$ rings: this chain is generated by translation and runs parallel to the [100] direction: four such chains run through each unit cell. The neutral water molecules are linked by O—H···O hydrogen bonds into continuous chains, running like sinuous rills throughout the structure, which themselves serve to link all the ionic chains into a single three-dimensional framework (Figs. 2–5).

In each of the four independent water molecules, one of the H atoms is fully ordered, but the other is disordered over two sites: careful inspection of difference maps showed that the alternative sites were, for each molecule, equally populated, and hence the s.o.f.s (site occupancy factors) of these disordered H atoms were subsequently all fixed at 0.5. The water molecules are hydrogen bonded into chains (Fig. 2), with two half-hydrogen sites between each pair of neighbouring O atoms (Table 2). The four-molecule chains are linked in a head-to-head fashion with pairs of molecules containing O3 linked across the inversion centres at (n, 0, 0) (n = zero or integer), and pairs of molecules containing O6 linked across the inversion centres at (0.5 + n, 0, 0) (n = zero or integer), so generating a continuous $C_4^4(8)$ chain running parallel to [100]; this chain thus runs along the line (x, 0, 0), albeit in a zigzag fashion, and there is a symmetry-related chain running similarly along the line $(x, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). The water chains thus run parallel to the [100] chain formed by the ionic components,

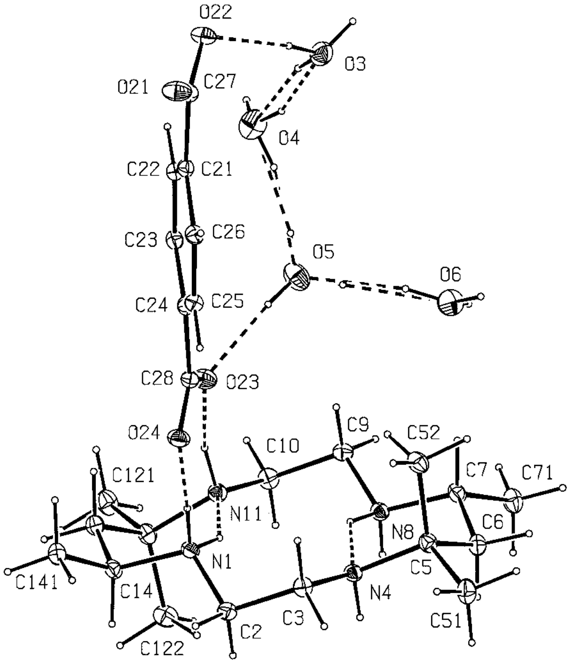


Figure 1
A view of the asymmetric unit in (1) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

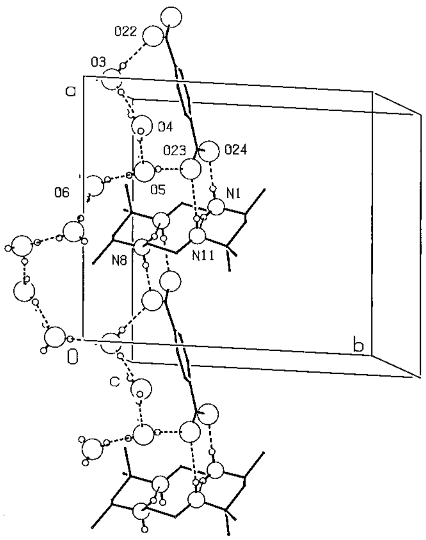


Figure 3
Part of the crystal structure of (1), showing the two types of chain parallel to [100]. For the sake of clarity H atoms bonded to C are omitted; unattached hydrogen bonds arise from N atoms in the cations.

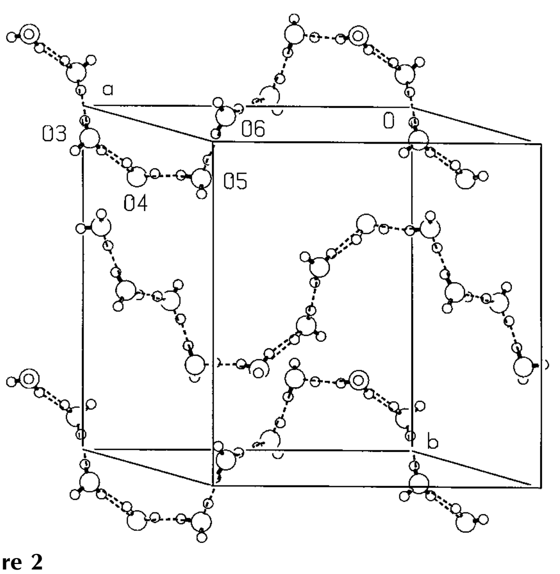


Figure 2
Part of the crystal structure of (1), showing the water chains along (x, 0, 0), $(x, \frac{1}{2}, \frac{1}{2})$ and (x, 1, 0). H atom sites within the chains all have occupancy $\frac{1}{2}$; those pendent from the chains all have occupancy 1.0.

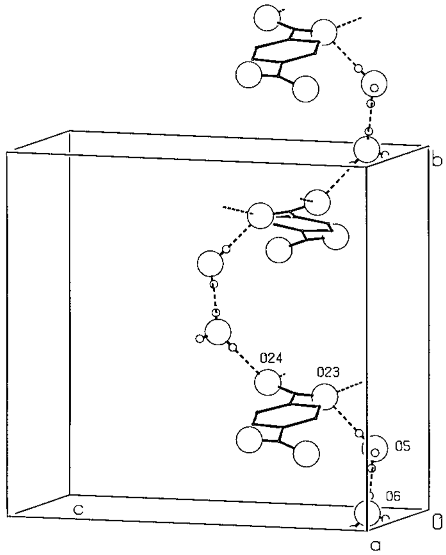


Figure 4
Part of the crystal structure of (1), showing one of the chains parallel to [010]. For the sake of clarity H atoms bonded to C are omitted; unattached hydrogen bonds arise from N atoms in the cations.

and alongside one repeat unit of the ionic chain there are two units of the water chain, containing eight water molecules (Fig. 3).

It may be assumed that at the local level only one of the H sites between each pair of O atoms is occupied at any instant: simultaneous occupation of both would not only disrupt the hydrogen bonding, but would require the two H atoms concerned to be within covalent bonding distance of one another. Instantaneous occupation of either H site between a given pair of O atoms thus precludes occupation of the other. If it is further assumed that the O atom in each water molecule forms, at any time, two and only two covalent bonds, then occupation of any one of the disordered sites within a particular chain necessarily defines the occupancy (unity or zero) of all other such sites within that chain. Hence, on this basis, the $\frac{1}{2}$ occupancy modelled from the X-ray diffraction data can be regarded as resulting from spacial averaging of the H site occupancy. It is also possible that there is temporal averaging: if the potential energy function describing the motion of a single H atom along the line between a pair of water O atoms exhibits two well defined equivalent minima, separated by a barrier insufficiently high to prevent tunnelling, then temporal averaging of the H sites will again reproduce the observed $\frac{1}{2}$ occupancy. Both spacial and temporal averaging mechanisms may be operating concurrently: in any event, at the local level the centres of inversion embedded within these chains must be a reflection of the overall averaging process.

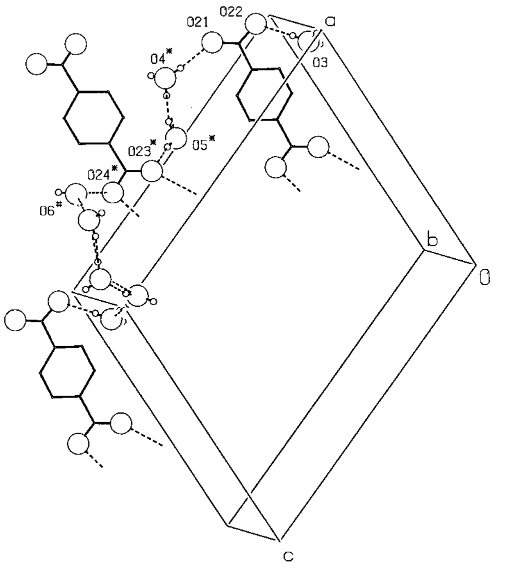


Figure 5
Part of the crystal structure of (1), showing one of the chains parallel to [001]. For the sake of clarity H atoms bonded to C are omitted; unattached hydrogen bonds arise from N atoms in the cations. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(2-x, -y, 1-z)$, respectively.

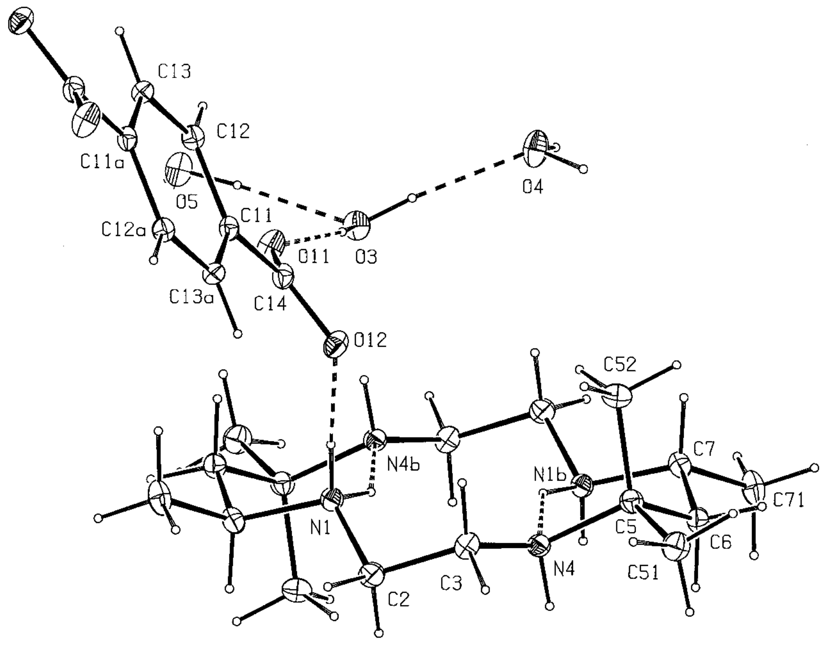


Figure 6
A view of the asymmetric unit in (2) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The ordered H atoms H*n*1 (*n* = 3–6) are pendent from the hydrogen-bonded chain of water molecules and these pendent H atoms serve to link all the chains built from cations and anions (Table 2). O3—H31 and O5—H51 in the molecules at (x, y, z) form hydrogen bonds to O22 and O23, respectively, within the same asymmetric unit, while O3—H31 and O5—H51 at $(1-x, -y, -z)$, *i.e.* in the next sector of the water chain, form corresponding hydrogen bonds to the phthalate anion at $(1-x, -y, -z)$, so linking two antiparallel ion chains related by centres of inversion. O4—H41 at (x, y, z) and O6—H61 at $(1-x, -y, -z)$ form hydrogen bonds to O21 and O24, respectively, in the phthalate anion at $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, while O6—H61 at (x, y, z) and O4—H41 at $(1-x, -y, -z)$ form hydrogen bonds to O24 and O21 in the phthalate anion at $(\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$: thus, O4 and O6 serve to link the original pair of antiparallel chains to a second similar pair, related to the first by the action of the glide planes. Hence, all four of the ionic [100] chains are linked through the agency of the water chains.

In addition to the two types of chain running parallel to [100] (Figs. 2 and 3) it is possible to identify chains parallel to both [010] and [001], all based upon the same phthalate anion at (x, y, z). The phthalate anion at (x, y, z) is linked, *via* the water molecules containing O5 and O6 also at (x, y, z) to the anion at $(\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, see Table 2: O23 in this anion is an acceptor from O5 at $(\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, which is linked *via* O6 at $(\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ to O24 in the anion at $(x, -1+y, z)$, so forming a spiral $C_3^3(8)$ chain running parallel to the [010] direction and generated by the 2_1 screw axis at $(\frac{3}{4}, y, \frac{1}{4})$ (Fig. 4). The same phthalate anion at (x, y, z) is linked *via* O3 at (x, y, z) and then *via* the four-molecule chain of water molecules at $(2-x, -y, -z)$ to the anion at $(\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, see Table 2: O23 in this anion is an acceptor from O5 at $(\frac{1}{2}+$

$x, \frac{1}{2} - y, -\frac{1}{2} + z$), which is linked *via* O4 at ($\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$) to O21 in the anion at ($x, y, -1 + z$), so generating a $C_9^9(22)$ chain parallel to [001] (Fig. 5).

Thus, there are chains running parallel to each of the [100], [010] and [001] directions, which link the phthalate anion at (x, y, z) directly to the anions at ($\pm1 + x, y, z$), ($x, \pm1 + y, z$) and ($x, y, \pm1 + z$), as well as linking together all four of the ionic chains running through each unit cell. Hence, the overall supramolecular architecture consists of a single three-dimensional framework propagating through the entire crystal: rather simple chains built from alternating cations and anions are linked into this framework by the continuous strings of water molecules.

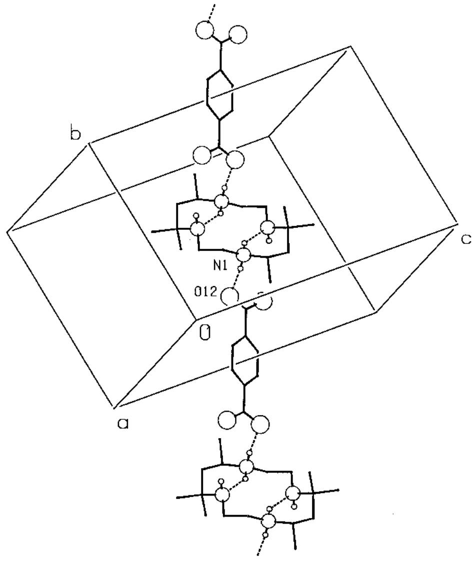


Figure 7
Part of the crystal structure of (2), showing one of the ionic chains running parallel to the [$1\bar{1}0$] direction. For the sake of clarity H atoms bonded to C are omitted.

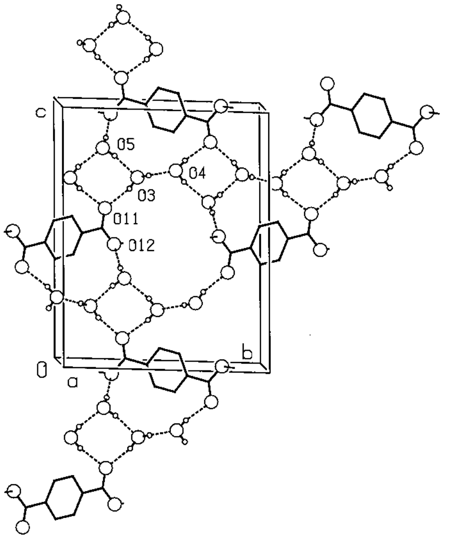


Figure 8
Part of the crystal structure of (2), showing part of one of the cation-free (100) nets arising from chains running parallel to [010] and [001] and built from $R_4^3(8)$, $R_4^4(15)$ and $R_8^8(20)$ rings. For the sake of clarity H atoms bonded to C are omitted; unattached hydrogen bonds arise from atoms N1 in the cations.

3.2.2. Compound (2). In (2) both organic components lie across centres of inversion; in addition, the structure contains three independent water molecules lying in general positions (Fig. 6). As in (1), the protons have been transferred from the terephthalic acid to the tet-a to form the salt $[C_{16}H_{38}N_4]^{2+}.[C_8H_4O_4]^{2-}.6H_2O$: in this salt the cation adopts the usual *trans*-III conformation (Barefield *et al.*, 1986). The reference cation lies across the centre of inversion at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and the anion across that at ($1, 0, \frac{1}{2}$), and in the cation, N1 at (x, y, z) acts as a hydrogen-bond donor to N4 at ($1 - x, 1 - y, 1 - z$) forming the usual (Gregson *et al.*, 2000) $R_2^2(10)$ motif within the N_4 cavity.

The organic components are linked by N—H···O hydrogen bonds into chains (Table 2 and Fig. 7). Atom N1 at (x, y, z), a component of the cation centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), acts as a hydrogen-bond donor to O12, also at (x, y, z), a component of the anion centred at ($1, 0, \frac{1}{2}$): the symmetry-related O12 in the same anion is at ($2 - x, -y, 1 - z$) and this atom is acceptor from N1, also at ($2 - x, -y, 1 - z$), which is a component of the cation centred at ($\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}$). This single type of N—H···O hydrogen bond combines with the intra-ring N—H···N hydrogen bond to generate a $C_3^3(6)$ [$R_2^2(10)$] chain-of-rings parallel to the [$1\bar{1}0$] direction (Fig. 7). The linking of the cations and anions is thus different for (1) and (2): in (1) each cation forms four N—H···O hydrogen bonds to a pair of anions, while in (2) each cation forms only two such bonds. The [$1\bar{1}0$] chain-of-rings utilizes one half of the organic components of the unit cell and it lies in the domain $\frac{1}{4} < z < \frac{3}{4}$: a second $C_3^3(6)$ [$R_2^2(10)$] chain-of-rings, related to the [$1\bar{1}0$] chain by the action of the 2_1 screw axes, runs parallel to [110] and lies in the domain $\frac{3}{4} < z < \frac{5}{4}$. The ionic components thus generate alternating rafts of [110] and [$1\bar{1}0$] chains, stacked alternately: these chains are linked by the water molecules into a three-dimensional framework.

The anions and the water molecules form a rather elaborate two-dimensional structure, most simply analysed in terms of two sets of chains intersecting to forming a net (Fig. 8). The water molecule at (x, y, z) and containing O3 acts as a hydrogen-bond donor both to O11 at (x, y, z), a component of the anion centred at ($1, 0, \frac{1}{2}$), and to the water molecule at (x, y, z) containing O4; this in turn acts as a donor to O11 at ($2 - x, \frac{1}{2} + y, \frac{3}{2} - z$), a component of the anion centred at ($1, \frac{1}{2}, 1$). Atom O11 at ($2 - x, \frac{1}{2} + y, \frac{3}{2} - z$) is also an acceptor from O3 at ($2 - x, \frac{1}{2} + y, \frac{3}{2} - z$), which acts as a donor to O4 at ($2 - x, \frac{1}{2} + y, \frac{3}{2} - z$), which in turn acts as a donor to O11 at ($x, 1 + y, z$), part of the anion centred at ($1, 1, \frac{1}{2}$). Thus, a $C_3^2(6)$ chain running parallel to the [010] direction is generated. This chain, however, exhibits some complexity: the O4 water molecule at ($2 - x, -\frac{1}{2} + y, \frac{3}{2} - z$) acts as a donor to both O11 and O5 at (x, y, z), and O5 at (x, y, z) also acts as a donor to O3 at (x, y, z), thus generating an almost square $R_4^3(8)$ ring (Fig. 8 and Table 2). Similar rings are generated by O4 at (x, y, z) acting as a donor to O5 and O11 at ($2 - x, \frac{1}{2} + y, \frac{3}{2} - z$), and so on: there is thus a chain of these $R_4^3(8)$ rings linked by O3—H···O(4) hydrogen bonds (Fig. 8). In between the $R_4^3(8)$ rings there are

$R_4^4(15)$ rings, so that the [010] motif is in fact a chain of fused rings in which the O5—H···O3 and O4—H···O11 hydrogen bonds form the ring junctions.

The [010] chain, which is generated by the 2_1 screw axis at $(1, y, \frac{3}{4})$, links the anion centred at $(1, \frac{1}{2}, 1)$ to those centred at $(1, 0, \frac{1}{2})$ and $(1, 1, \frac{1}{2})$. In the anion centred at $(1, \frac{1}{2}, 1)$, the O11 atom at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ accepts a hydrogen bond from O3, also at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$: the water molecule containing O5, also at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ is a hydrogen-bond donor both to O3 at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and to O12 at $(x, y, 1 + z)$. This sequence of hydrogen bonds thus generates a $C_3^3(8)$ chain running parallel to the [001] direction. As with the [010] chain, the [001] chain incorporates $R_4^3(8)$ and R_4^4 rings (Fig. 8). The [001] chain is generated by the glide plane at $y = \frac{1}{4}$ and it serves to link the anion centred at $(1, \frac{1}{2}, 1)$ to those centred at $(1, 0, \frac{1}{2})$ and $(1, 0, \frac{3}{2})$.

The arrangement of the anions and the water molecules can conveniently be viewed in two ways: one view is in terms of chains running parallel to [010] and [001] and generated, respectively, by a screw axis and a glide plane (Fig. 8). Alternatively, the action of the centres of inversion on any $C_3^2(6)$ segment of an [010] chain and on any $C_3^3(8)$ segment of an [001] chain generates two sets of intersecting chains running parallel to [011] and [01$\bar{1}$]. Whichever description is preferred, the end result is the formation of a two-dimensional cation-free substructure (Gregson *et al.*, 2000) in the form of a rhomboidal array of anions linked by water molecules lying parallel to (100) and built from a fused series of $R_4^3(8)$, $R_4^4(15)$ and $R_8^8(20)$ rings, the last type of which is centrosymmetric (Fig. 8). Just one of these (100) nets runs through each unit cell, but this stack of nets is intersected and interconnected by the ionic chains along [110] and [1$\bar{1}$0] (Fig. 7): in effect the (100) nets are tied together by the $[(\text{tet-a})H_2]^{2+}$ cations, to form a single three-dimensional framework.

3.2.3. General comments of the supramolecular structures of (1) and (2). In $[(\text{tet-a})H_2]^{2+}$cations the two N atoms giving rise to the pair of axial N—H bonds on a given face are typically separated by 2.8–2.9 Å. In an aryl carboxylate anion, on the other hand, the two O atoms are typically separated by *ca* 2.3–2.4 Å, and inasmuch as hard hydrogen bonds are commonly found with *D*—H···*A* angles around 160°, a carboxylate anion acting as a double acceptor of hydrogen bonds should fit rather neatly across a pair of axial N—H bonds in $[(\text{tet-a})H_2]^{2+}$, acting as hydrogen-bond donors. Thus, if a bis-carboxylate anion were to engage its two COO^- groups with paired N—H bonds in two different $[(\text{tet-a})H_2]^{2+}$ cations, while different carboxylate di-anions were hydrogen-bonded to the two faces of a given cation, chain formation would result. In such a chain the strength of the N—H···O hydrogen bonds should be enhanced by the fact that both donor and acceptor are ionic (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994).

In the event, this neat fitting of the carboxylate acceptor to the cationic donor by means of paired N—H···O hydrogen bonds is attained only in (1): it does not occur in (2) or indeed in the corresponding salts formed by tet-a with 3- and 4-hydroxybenzoic acids or with 3,5-dihydroxybenzoic acid (Gregson *et al.*, 2000). What appears to be an ideally complementary pairing of donors and acceptors, and thus a potentially useful synthon for supramolecular design, is in fact realized only occasionally and unpredictably in a series of closely related salts. Even in (1) and (2) described above (§§3.2.1 and 3.2.2), whose constitutions differ only in the degree of hydration, the N—H···O hydrogen-bonding patterns are very different. The hydrogen-bonding behaviour in (1) therefore represents an apparent anomaly in the series of tet-a/carboxylic acid systems so far investigated: (1) also represents the only example in this series in which the $[(\text{tet-a})H_2]^{2+}$ cations do not lie across centres of inversion.

Multi-component three-dimensional frameworks can generally be described in a variety of ways. The simplest description of (2) is that in terms of the two-dimensional cation-free substructure, with cation-free nets linked by the ionic chains: a similar descriptive approach, in terms of a substructure of lower dimensionality and containing a limited set of the molecular components, has proved extremely helpful in analysing the supramolecular structures of other multi-component systems of similar type (Gregson *et al.*, 2000; Glidewell *et al.*, 2000).

The linking of water molecules by means of O—H···O hydrogen bonds into continuous strings, as observed in (1) is, in fact, a rather common motif in organic hydrates. A search of the April 1999 release of the Cambridge Structural Database (Allen & Kennard, 1993) for systems containing at least four water molecules thus linked produced over 60 hits for the period 1991 onwards. In a number of cases this feature was not commented upon in the original structure report, although such continuous chains are discussed, for example, by Caira *et al.* (1994), Mootz *et al.* (1994) and Kumar *et al.* (1995). Effectively square $R_4^4(8)$ rings of four water molecules, somewhat similar to the $R_4^3(8)$ rings observed in (2), have also been reported (Bujak *et al.*, 1998).

3.3. Hydrogen-bond dimensions

It has recently been noted that the criteria for acceptance of non-covalent contacts involving hydrogen as genuine hydrogen bonds seem to be undergoing continual relaxation (Cotton *et al.*, 1997). It therefore seems desirable to specify the acceptance criteria adopted here for the hydrogen bonds listed in Table 2. In (1) and (2) the O—H···O hydrogen bonds have O···O distances in the range 2.749 (2)–2.930 (2) Å with O—H···O angles closely clustered around 170°. The N—H···O hydrogen bonds have N···O distances in the range 2.719 (2)–3.260 (2) Å and with the exception of a single outlying value in (1), the N—H···O angles are also clustered closely around 170°: the outlying value, N11···O23 in (1), has both the longest N—O distance and the smallest N—H···O angle, both by some margin, and thus may be confidently regarded as the weakest of the N—H···O hydrogen bonds amongst those in Table 2. However, the paired nature of the N—H···O hydrogen bonds in (1) means that, even if this N11···O23 bond were to be disregarded, there would be no material change to the description of the supramolecular structure.

3.4. Molecular dimensions and conformations

In (2) both organic components lie across centres of inversion, whereas in (1) both lie in general positions. Despite this difference, the leading dimensions of these organic ions in the two structures are very similar (Table 3). The dimensions of the cation in (1), where the bond lengths, inter-bond angles and torsional angles of the peripheral skeleton all indicate a structure and conformation which is very close to being centrosymmetric: the values of the torsional angles in the two corresponding sectors of the cation periphery (N1–C10) and (N8–C3) are particularly striking. Moreover, the dimensions, including the torsional angles, are extremely close to those found in (2). Entirely similar remarks apply to the geometry of the anions.

4. Conclusions

Terephthalic acid and tet-a form a 1:1 ionic adduct, as anticipated from earlier studies: unexpected was the isolation of two different hydrates, the tetrahydrate (1) and the hexahydrate (2), from rather similar co-crystallization procedures: the structure analyses show that these hydrates have entirely different three-dimensional structures, but that in each case rather simple principles of structure description apply. In (1) distinct chains can be identified built from the ionic components on the one hand, and the water molecules on the other: in (2), a two-dimensional substructure can be identiifed, built from water molecules and anions only.

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