

Hydrogen-bonded sheets in the 1:1 salt of tet-b and trimesic acid

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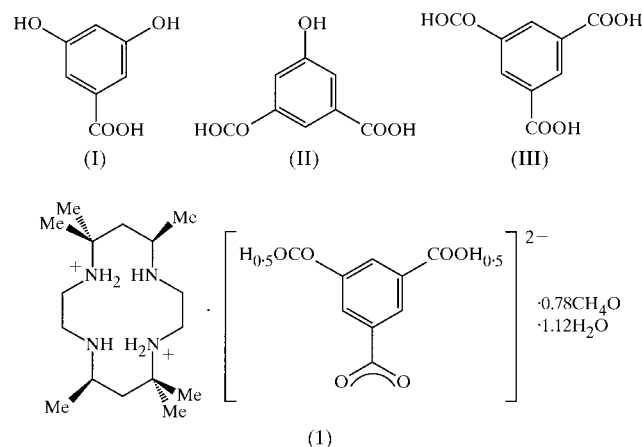
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Tet-b (racemic 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $C_{16}H_{36}N_4$) and trimesic acid (1,3,5-benzenetricarboxylic acid, $C_9H_6O_6$) form a salt partially solvated by both water and methanol, *i.e.* 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–1,3,5-benzenetricarboxylic acid–methanol–water (1/1/0.78/1.12), $C_{16}H_{38}N_4^{2+} \cdot C_9H_4O_6^{2-} \cdot 0.78CH_4O \cdot 1.12H_2O$. The anions are linked by O–H...O hydrogen bonds [O...O 2.442 (4) and 2.458 (4) Å; O–H...O 170 and 171°] into zigzag chains; orientationally disordered cations are linked to the anion chains by means of N–H...O hydrogen bonds [major orientation: N...O 2.695 (3)–3.071 (4) Å, N–H...O 148–179°; minor orientation: N...O 2.75 (2)–3.34 (2) Å, N–H...O 147–170°] and link the chains into sheets. The solvent molecules are all disordered, but appear to play no significant structural role apart from space filling.

Comment

The *meso* form of the tetraaza macrocycle 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-a), $C_{16}H_{36}N_4$, forms a salt with the trigonally trisubstituted benzenecarboxylic acid 3,5-dihydroxybenzoic acid, (I), in which $[(HO)_2C_6H_3COO]^-$ anions form hydrogen-bonded sheets which are linked by the $[(tet-a)H_2]^{2+}$ ($C_{16}H_{38}N_4^{2+}$) dications into a continuous three-dimensional framework based on a pillared-layer architecture (Gregson *et al.*, 2000). With the closely related acid 5-hydroxyisophthalic acid, (II), both the *meso* (tet-a) and racemic (tet-b) forms of this tetraaza macrocycle form hydrated salts in which the overall supramolecular structure is two-dimensional, with chains built from anions and water molecules linked together by $[(tet-b)H_2]^{2+}$ dications (Burchell *et al.*, 2000). Continuing this study, we have now investigated the behaviour of the racemic form tet-b with

the symmetrically trisubstituted acid 1,3,5-benzenetricarboxylic acid [trimesic acid, $C_9H_6O_6$, (III)]. The 1:1 adduct, *i.e.* (1), formed between tet-b and acid (III) proves to be the salt $C_{16}H_{38}N_4^{2+} \cdot C_9H_4O_6^{2-}$, solvated by both water and methanol. The supramolecular structure consists of two-dimensional hydrogen-bonded sheets in which the solvent molecules play no significant part.



The cation (Fig. 1) is protonated at N14 and N11; the two additional H atoms, captured from the acid, are fully ordered and participate in intramolecular N–H...N hydrogen bonds. The cation in adduct (1) is orientationally disordered, with approximately one eighth of the cation sites containing an orientation in which the cation is rotated by *ca* 180° about a

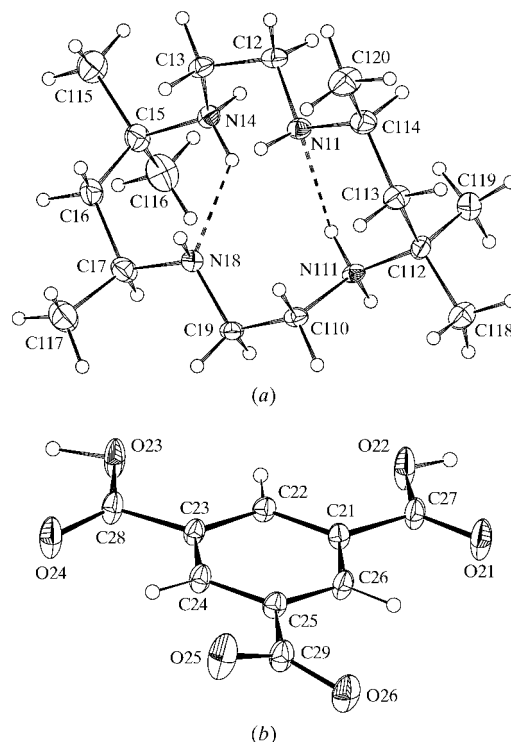


Figure 1

The major ionic components of adduct (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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line through the midpoints of the vectors $N11 \cdots N14$ and $N18 \cdots N111$ (Fig. 2). The conformation of the cation, which is the same for both the major and minor orientations, is that previously observed for $[(\text{tet-}b)\text{H}_2]^{2+}$ (Simonov *et al.*, 1998; Burchell *et al.*, 2000), with the four N atoms approaching a

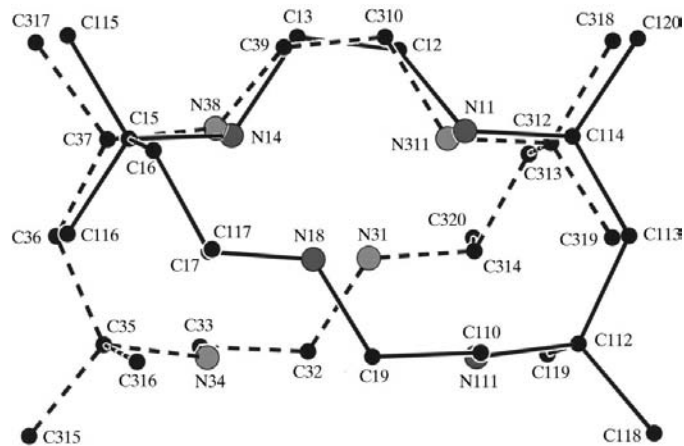


Figure 2

The major (N11, N14, N18 and N111) and minor (N31, N34, N38 and N311) orientations of the cation. C and N atoms are depicted as spheres of arbitrary radii, and H atoms have been omitted for clarity.

tetrahedral arrangement. Although the cation lies in a general position, the magnitudes and signs of the dihedral angles around the ring periphery (Table 1) indicate that the cation has close to C_2 rotational symmetry (Figs. 1 and 2). In contrast, the $[(\text{tet-}a)\text{H}_2]^{2+}$ cation is generally centrosymmetric (Gregson *et al.*, 2000), so that its four N atoms are strictly coplanar. Within the cation, there are clear differences in the C–N bond lengths involving protonated or unprotonated N atoms, respectively, with those involving protonated N atoms being significantly longer (Table 1). For the longer C–N bonds, there is, in addition, a clear dependence on the degree of substitution of the C atom involved; the N(H)–CH₂ bonds have a mean length of 1.493 (6) Å, while the N(H)–CMe₂ bonds have a mean length of 1.525 (6) Å.

In the $\text{C}_9\text{H}_4\text{O}_6^{2-}$ anion (Fig. 1), the remaining carboxylic acid H atom is disordered over two sites, adjacent to O22 and O23, with equal occupancy. The C–O bond lengths (Table 1) are fully consistent with these locations for this H atom. It was found from difference maps that the O22–H222 distance was normal at 0.85 Å, while the O23–H223 distance was longer at 1.10 Å.

The two-dimensional supramolecular structure of adduct (1) is most readily analysed and described using the substructure approach (Gregson *et al.*, 2000). The anions form

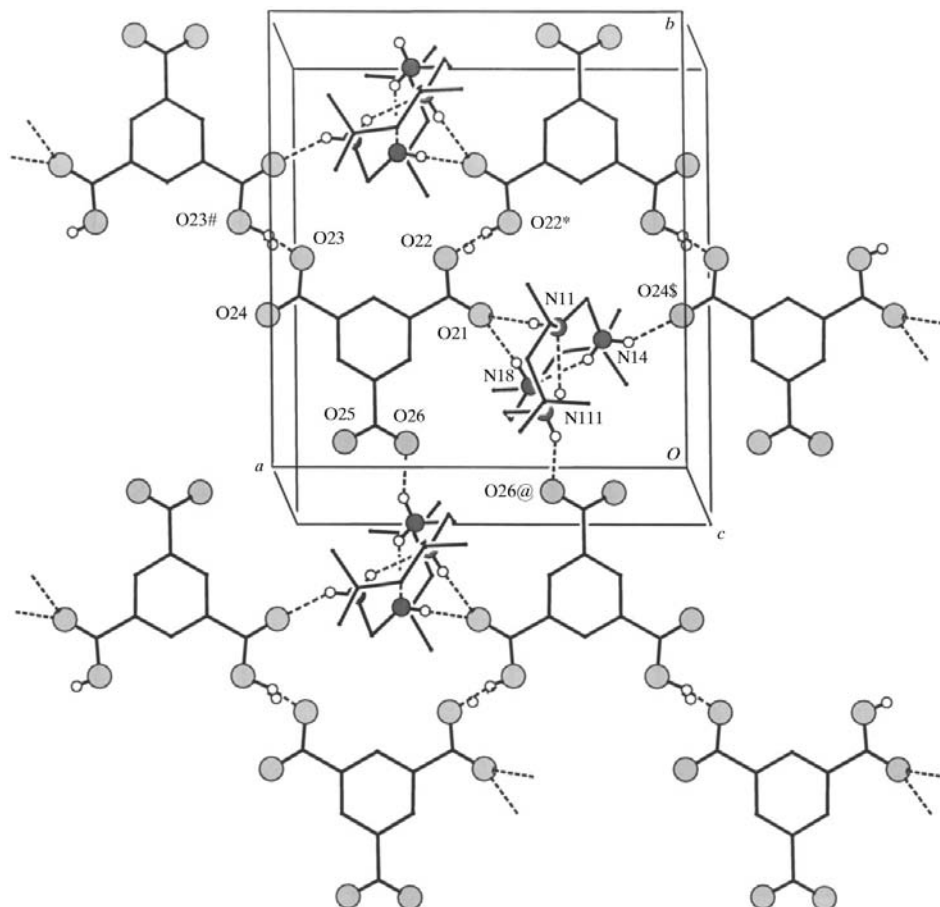


Figure 3

Part of the crystal structure of (1) showing the anion chains parallel to [100] linked into (001) sheets by the cations. Atoms marked with an asterisk (*), hash (#), dollar (\$) or at (@) sign are at the symmetry positions $(1-x, 1-y, -z)$, $(2-x, 1-y, -z)$, $(-1+x, y, z)$ and $(1-x, -y, -z)$, respectively.

hydrogen-bonded chains, which are linked into sheets by the cations. Each anion is linked to two further anions by means of O—H···O hydrogen bonds; O22 at (x, y, z) acts as donor to O22 at $(1-x, 1-y, -z)$, while O23 at (x, y, z) acts as donor to O23 at $(2-x, 1-y, -z)$, and these hydrogen bonds generate zigzag chains parallel to the [100] direction (Fig. 3). Averaged over the entire structure, each close inter-anion O···O contact involves two half-H atoms, but at the local level, a given O···O contact can only involve a single H atom; if both H sites were occupied, the H atoms would be within covalent bonding distance. Hence, the carboxyl H-atom locations within each [100] chain must be correlated, but there is no correlation between adjacent chains.

Each cation takes part in four N—H···O hydrogen bonds; the hydrogen-bonding behaviour of the two orientations is similar (Table 2) and only that of the major orientation will be discussed. Both N11 and N18 act as donors, *via* H11A and H18A, respectively, to O21 within the asymmetric unit, and N14 acts as donor, *via* H14F, to O24 in the anion at $(-1+x, y, z)$; this anion is a component of the same [100] chain, running along the line $(x, \frac{1}{2}, 0)$, as the cation and anion at (x, y, z) . N111, however, acts as donor, *via* H11C, to O26 in the anion at $(1-x, -y, -z)$, which is a component of the [100] chain along the line $(x, -\frac{1}{2}, 0)$. In this manner, each cation links two adjacent [100] chains, producing a continuous sheet parallel to (001) (Fig. 3). Two such sheets pass through each unit cell, one in the domain $-0.27 < z < 0.27$, and the other in the domain $0.23 < z < 0.77$. There are neither hydrogen bonds nor aromatic π - π stacking interactions between adjacent (001) sheets. The overall structure is thus reminiscent of those found in the salts of both tet-a and tet-b with 5-hydroxyisophthalic acid (Burchell *et al.*, 2000), with anion chains linked into sheets by cations.

Although elemental analysis originally suggested that adduct (1) contained two molecules of methanol per ion pair, the structure analysis reported here has shown that there are also present in the structure two partial methanol molecules and three partial water molecules. The major methanol component (O41—C42) acts as a hydrogen-bond donor, and is pendent from the anion chain (Table 2). For the rest of the solvent molecules, no H atoms at all could be located, presumably because of disorder and/or mobility of these components, so that no comment can be made upon any structural role they might have. It is possible that the incorporation of the solvent is largely adventitious, with the solvent molecules occupying what would otherwise be minor voids in the structure.

The structure reported here is characterized by several forms of disorder: firstly, there is the orientational disorder of the cations; secondly, there is the carboxylic acid H-atom disorder in the anions; and finally, there is the solvent disorder, involving both partial site occupancy and possible orientational disorder. These various forms of disorder allied with the poor crystal quality undoubtedly contribute to the somewhat high *R* value; nonetheless, the study presented here demonstrates that even apparently intractable systems will yield, given care and persistence.

Experimental

A sample of tet-b was prepared, as the monohydrate, according to the literature method of Hay *et al.* (1975). Equimolar quantities of tet-b and of the acid (III) were separately dissolved in methanol and set aside to crystallize, exposed to the laboratory atmosphere, producing solvated (1). Analysis: found C 57.9, H 9.1, N 10.0%; $C_{27}H_{50}N_4O_8$ [(1)·2MeOH] requires C 58.0, H 9.0, N 10.0%; $C_{25.78}H_{47.36}N_4O_{7.90}$ [(1)·0.78MeOH·1.12H₂O] requires C 57.4, H 8.8, N 10.4%. Crystals just adequate for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_{16}H_{38}N_4^{2+} \cdot C_9H_4O_6^{2-} \cdot 0.78CH_4O \cdot 1.12H_2O$
 $M_r = 539.80$
 Monoclinic, $P2_1/n$
 $a = 13.8921$ (9) Å
 $b = 15.3390$ (6) Å
 $c = 14.0209$ (8) Å
 $\beta = 95.666$ (2)°
 $V = 2973.1$ (3) Å³
 $Z = 4$

$D_x = 1.206$ Mg m⁻³
 Mo K α radiation
 Cell parameters from 33 988 reflections
 $\theta = 2.55$ – 25.00 °
 $\mu = 0.089$ mm⁻¹
 $T = 150$ (2) K
 Needle, colourless
 $0.30 \times 0.12 \times 0.12$ mm

Data collection

KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{min} = 0.974$, $T_{max} = 0.989$
 33 988 measured reflections
 5228 independent reflections

3154 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.051$
 $\theta_{max} = 25$ °
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 18$
 $l = -16 \rightarrow 16$
 Intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.077$
 $wR(F^2) = 0.212$
 $S = 0.986$
 5228 reflections
 427 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0984P)^2 + 2.1918P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.004$
 $\Delta\rho_{max} = 0.34$ e Å⁻³
 $\Delta\rho_{min} = -0.21$ e Å⁻³

Compound (1) is monoclinic and space group $P2_1/n$ was uniquely determined from the systematic absences. The crystal quality was poor and several crystals were used during the data collection. Two

Table 1
 Selected geometric parameters (Å, °).

N11—C12	1.467 (5)	N111—C112	1.520 (5)
N11—C114	1.460 (5)	O21—C27	1.231 (4)
N14—C13	1.499 (6)	O22—C27	1.276 (4)
N14—C15	1.530 (6)	O23—C28	1.278 (4)
N18—C17	1.467 (5)	O24—C28	1.230 (4)
N18—C19	1.473 (4)	O25—C29	1.255 (4)
N111—C110	1.487 (4)	O26—C29	1.248 (4)
N11—C12—C13—N14	−67.0 (5)	N111—C112—C113—C114	−67.3 (6)
C12—C13—N14—C15	174.4 (5)	C112—C113—C114—N11	56.2 (6)
C13—N14—C15—C16	−71.3 (7)	C113—C114—N11—C12	−167.2 (4)
N14—C15—C16—C17	−64.0 (5)	C114—N11—C12—C13	−170.0 (4)
C15—C16—C17—N18	62.5 (5)	C22—C21—C27—O21	−178.5 (3)
C16—C17—N18—C19	−176.2 (3)	C22—C21—C27—O22	0.7 (5)
C17—N18—C19—C110	−174.9 (3)	C22—C23—C28—O23	−8.4 (5)
N18—C19—C110—N111	−67.6 (4)	C22—C23—C28—O24	169.6 (3)
C19—C110—N111—C112	174.6 (3)	C24—C25—C29—O25	−16.9 (5)
C110—N111—C112—C113	−59.8 (4)	C24—C25—C29—O26	163.3 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N14—H14E...N18	0.92	2.17	2.878 (9)	133
N111—H11C...N11	0.92	2.24	2.880 (5)	126
N11—H11A...O21	0.92	2.08	3.002 (6)	179
N14—H14F...O24 ⁱ	0.92	2.03	2.853 (9)	148
N18—H18A...O21	0.92	2.16	3.071 (4)	169
N111—H11D...O26 ⁱⁱ	0.92	1.85	2.695 (3)	152
O22—H22...O22 ⁱⁱⁱ	0.85	1.62	2.458 (4)	171
O23—H23...O23 ^{iv}	1.10	1.35	2.442 (4)	170
O41—H41...O25	0.84	1.81	2.643 (4)	172
N34—H34A...N38	0.92	2.33	2.94 (4)	124
N311—H31C...N31	0.92	2.11	2.84 (5)	136
N31—H31A...O24 ⁱ	0.92	2.47	3.34 (2)	158
N34—H34B...O25 ⁱⁱ	0.92	1.91	2.75 (2)	152
N38—H38A...O24 ⁱ	0.92	1.91	2.82 (7)	170
N311—H31D...O21	0.92	2.29	3.10 (4)	147

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, -y, -z$; (iii) $1-x, 1-y, -z$; (iv) $2-x, 1-y, -z$.

complete data sets were collected at 150 K and that employed here was marginally the better; both sets had rather high merging *R* factors. It was apparent at an early stage of refinement that the cation was disordered over two sites but that the two orientations had essentially the same conformation; the site-occupation factors (s.o.f.'s) for the major and minor forms of the cations refined to 0.839 (3) and 0.161 (3), respectively. The minor component was refined isotropically, with a common isotropic displacement parameter for the N atoms, a second parameter for all the ring C atoms and a third for the methyl C atoms. In addition to the ionic components, two partial methanol molecules were located; one (O41—C42) had an s.o.f. of 0.700 (7) and all its H atoms were located from difference maps, the other (O51—C52) had an s.o.f. of 0.084 (4), but its H atoms could not be located. There were also three partial water molecules present; the O atoms for two of them, O61 and O62, were very close together and their s.o.f.'s [0.896 (6) and 0.104 (6)] were constrained to sum to unity, while the s.o.f. of the third, O71, refined to 0.116 (5). Despite extensive searches, no water H atoms could be

found, even for O61. The carboxyl H atoms in the anion occupied two sites, with equal occupancy: H222 was located at a normal distance from O22 and was treated as riding with O—H = 0.85 Å, but the other, H223, was clearly more distant from O23 and was treated as riding with O—H = 1.10 Å. All other identified H atoms were treated as riding, with N—H = 0.92 Å and C—H = 0.95 (aromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic CH).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL97* and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC (Canada).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1438). Services for accessing these data are described at the back of the journal.

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