

## A three-dimensional hydrogen-bonded framework in 4,4'-trimethylenedipiperidinium–2,5-dicarboxybenzene-1,4-dicarboxylate–water (1/1/1)

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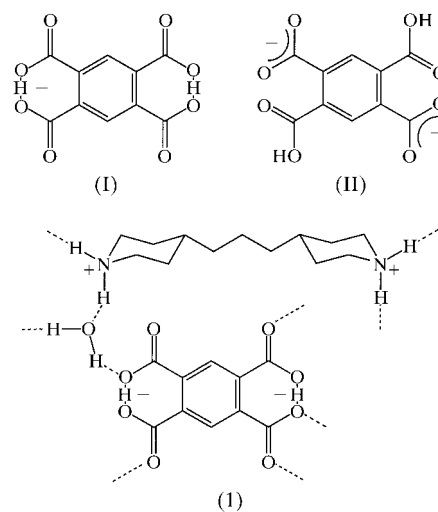
The title compound is a salt,  $C_{13}H_{28}N_2^{2+} \cdot C_{10}H_4O_8^{2-} \cdot H_2O$ . In the anion, there are two short intramolecular hydrogen bonds [ $O \cdots O$  2.395 (2) and 2.383 (2) Å;  $O \cdots H \cdots O$  175 and 172°]. Pairs of anions and pairs of water molecules are linked by further  $O-H \cdots O$  hydrogen bonds [ $O \cdots O$  2.756 (2) and 2.980 (2) Å;  $O-H \cdots O$  171 and 175°] into cyclic centrosymmetric  $R_6^6(16)$  aggregates; these aggregates are linked *via* the cations into a three-dimensional framework by means of four distinct  $N-H \cdots O$  hydrogen bonds [ $N \cdots O$  2.787 (2)–3.204 (2) Å;  $N-H \cdots O$  148–173°].

### Comment

Benzene-1,2,4,5-tetracarboxylic acid [ $C_6H_2(COOH)_4$ , pyromellitic acid] readily forms an anion,  $[C_{10}H_4O_8]^{2-}$ , and the behaviour of this anion in the solid state is dominated by two distinct patterns of hydrogen bonding (Lough *et al.*, 2000). In form (I), there are two intramolecular hydrogen bonds which are very short, with  $O \cdots O$  distances around 2.40 Å and with the H atom nearly, or exactly, centred along the  $O \cdots O$  vector; this isomer can thus act only as an acceptor of hard intermolecular hydrogen bonds. In the alternative form (II), there are no intramolecular hydrogen bonds so that it can act both as a twofold donor of hydrogen bonds and as a multiple acceptor.

Continuing our earlier structural study (Lough *et al.*, 2000) of salts formed between this acid and organic diamines, we have now characterized a hydrated salt formed with the chain-extended diamine 4,4'-trimethylenedipiperidine  $HNC_5H_9-(CH_2)_3-C_5H_9NH$ ; double protonation of this amine will provide a chain-extended  $[H_2NC_5H_9-(CH_2)_3-C_5H_9NH_2]^{2+}$  dication capable of acting as a fourfold donor of hydrogen bonds, while the distance between the two  $NH_2$  units can provide an effective spacer between the anionic components.

The title compound is a hydrated salt,  $[C_{13}H_{28}N_2]^{2+} \cdot [C_{10}H_4O_8]^{2-} \cdot H_2O$ , (1), in which each of the components lies in a general position (Fig. 1). The anion adopts form (I) with two intramolecular hydrogen bonds and acts as a fivefold acceptor of intermolecular hydrogen bonds; the cation acts as a fourfold donor, and the neutral water molecule acts as a double donor and as a single acceptor of hydrogen bonds. There are thus six distinct intermolecular hydrogen bonds, four of the  $N-H \cdots O$  type and two of the  $O-H \cdots O$  type (Table 2). These link the components into a single three-dimensional framework. While frameworks containing so many different hydrogen bonds can generally be described in a large number of ways, the supramolecular structure of (1) is most simply described in terms of the formation of finite clusters of anions and water molecules, and the subsequent linking of these clusters by the cations.



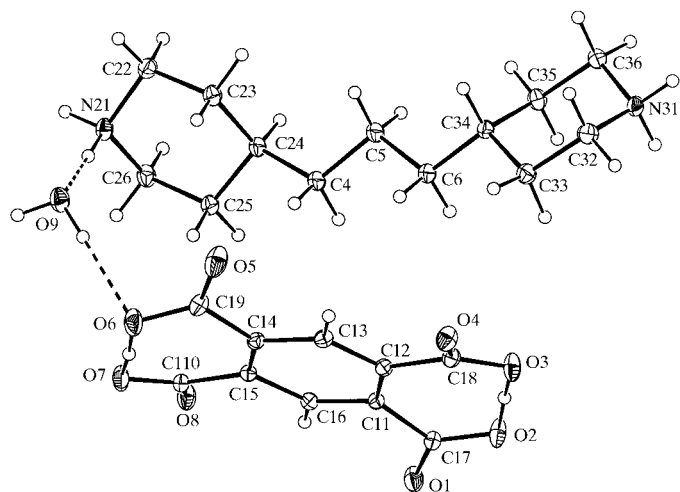
Pairs of anions and pairs of water molecules form cyclic centrosymmetric aggregates. The water molecule at  $(x, y, z)$  acts as donor, *via* H91, to O6 also at  $(x, y, z)$  and, *via* H92, to O8 at  $(1-x, 1-y, 1-z)$ , thus generating a centrosymmetric  $R_6^6(16)$  motif (Fig. 2). There is one of these four-component aggregates at the centre of each unit cell, so that the cell contains two anions and two water molecules. The linking of the clusters by the cations can itself be conveniently described in two steps.

The cations link the anion/water clusters into chains of fused rings running parallel to the [001] direction, by the action of N21 as a double donor of hydrogen bonds, while hydrogen bonds having N31 as donor link the [001] chain into a continuous framework. Atom N21 at  $(x, y, z)$  is a donor, *via* H21A, to O9 at  $(x, y, z)$  and, *via* H21B, to O4 at  $(x, y, -1+z)$ ; N21 at  $(1-x, 1-y, -z)$  likewise acts as donor to O9 at  $(1-x, 1-y, -z)$  and to O4 at  $(1-x, 1-y, -1-z)$ . In this manner, a centrosymmetric  $R_6^6(26)$  ring is formed: in the [001] chain, the  $R_6^6(16)$  rings are centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + n)$  and the  $R_6^6(26)$  rings at  $(\frac{1}{2}, \frac{1}{2}, n)$  ( $n = \text{zero or integer}$ ) (Fig. 2), and a single chain of this type runs through each unit cell.

The N31 donors pendent from chains of this type link all the chains together. N31 at  $(x, y, z)$  is a component of the chain along  $(\frac{1}{2}, \frac{1}{2}, z)$ : it acts as donor, *via* H31A, to O1 at  $(-1+x, 1+y, z)$ , which is a component of the chain along  $(-\frac{1}{2}, \frac{3}{2}, z)$ ,

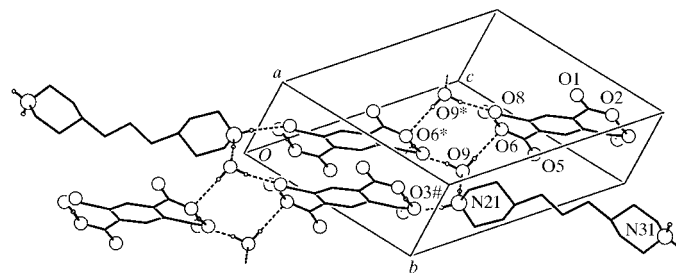
and, *via* H31B, to O2 at  $(1-x, 2-y, 2-z)$  which is a component of the chain along  $(\frac{1}{2}, \frac{3}{2}, z)$ . Propagation of these links by inversion and translation serves to join all the [001] chains into a continuous framework.

In each of the two independent intramolecular hydrogen bonds in the anion, the H atom is equidistant from the O atoms and  $O \cdots H \cdots O$  is almost linear (Table 2). The formation of these short strong hydrogen bonds evidently occurs at some energy cost to the rest of the anion, as manifested in geometric distortion elsewhere in the anion. Not only are all the  $-COO^-$  units significantly twisted out of the plane of the aryl ring (Table 1), but the exocyclic C–C–C bond angles within the *S*(7) ring are all just above  $128^\circ$ , indicative of considerable steric strain. The rotations of the carboxylate substituents are concerted (Table 1). The rotations of the pairs containing C17 and C18, and C19 and C110 are disrotatory, while those of the pairs containing C18 and C19, and C17 and C110 are conrotatory. The molecular symmetry of the anion is thus approximately  $C_{2h}$  ( $2/m$ ) rather than the optimum  $D_{2h}$  ( $mmm$ ), with the approximate twofold axis running through the two C–H bonds. The same, approximately  $C_{2h}$ , conformation is observed for each of the two independent  $[C_{10}H_4O_8]^{2-}$  anions in the salt with monoprotonated hexamethylenetetramine and, indeed, one of these anions lies across a centre of inversion (Lough *et al.*, 2000), while in the salt  $[Ni(H_2O)_6]^{2+} \cdot [C_{10}H_4O_8]^{2-}$ , the anions lie in special positions of  $2/m$  symmetry (Jessen *et al.*, 1992). In the 1:1 salt formed from 2,2'-bipyridyl,  $[(C_{10}H_8N_2)H]^+ \cdot [C_{10}H_4O_8]^{2-} \cdot [C_{10}H_6O_8]$ , where the carboxylate rotations in the centrosymmetric anion again generate approximate  $C_{2h}$  symmetry, it is now the approximate mirror plane which contains the two C–H bonds (Mrvoš-Sermek *et al.*, 1996). In each of the substituents, the C–O bond involved in the intramolecular hydrogen bond is very much longer than its companion, by between 0.048 (2) and 0.077 (2) Å, indicative of some bond fixation within the carboxylate groups; of the C–O bonds not so involved, C19–O5, where the O is not involved in either inter- or intramolecular hydrogen bonding, is significantly shorter than the remainder.



**Figure 1**  
The asymmetric unit of (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

In the cation, the two independent rings both adopt chair conformations with the central  $-(CH_2)_3-$  spacer unit occupying equatorial sites in both; this spacer has an extended all-*trans* conformation, and the cation as a whole has approximate  $C_2$  symmetry. There is a long sequence of antiperiplanar torsion angles between C26 and C32, all within  $10^\circ$  of  $180^\circ$  (Table 1 and Fig. 1). The similar magnitudes of the torsion angles C23–C24–C4–C5 and C35–C34–C6–C5 and their identical signs confirm the approximate  $C_2$  symmetry. The bond lengths and angles in the cation all have normal values.



**Figure 2**  
Part of the crystal structure of (1), showing linking of the anion/water aggregates by the cations into a chain of alternating  $R_6^o(16)$  and  $R_6^o(26)$  rings along [001]. Atoms marked with a star (\*) and hash (#) are at the symmetry positions  $(1-x, 1-y, 1-z)$  and  $(x, y, -1+z)$ , respectively.

## Experimental

Equimolar quantities of 4,4'-trimethylenedipiperidine and benzene-1,2,4,5-tetracarboxylic acid dihydrate were separately dissolved in methanol. The solutions were mixed and the mixture was set aside to crystallize, producing analytically pure (1). Analysis: found C 57.4, H 7.0, N 5.8%;  $C_{23}H_{34}N_2O_9$  requires C 57.2, H 7.1, N 5.8%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

### Crystal data

$C_{13}H_{28}N_2^{2+} \cdot C_{10}H_4O_8^{2-} \cdot H_2O$   
 $M_r = 482.52$   
 Triclinic,  $P\bar{1}$   
 $a = 10.5885$  (4) Å  
 $b = 11.5840$  (6) Å  
 $c = 11.8301$  (6) Å  
 $\alpha = 61.453$  (2)°  
 $\beta = 80.999$  (3)°  
 $\gamma = 64.055$  (3)°  
 $V = 1143.63$  (9) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.401$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8817 reflections  
 $\theta = 2.81$ – $30.07^\circ$   
 $\mu = 0.108$  mm<sup>-1</sup>  
 $T = 150$  (1) K  
 Block, colourless  
 $0.31 \times 0.26 \times 0.16$  mm

### Data collection

KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)  
 $T_{\min} = 0.967$ ,  $T_{\max} = 0.983$   
 8817 measured reflections  
 6632 independent reflections

4752 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$   
 $\theta_{\text{max}} = 30.07^\circ$   
 $h = 0 \rightarrow 14$   
 $k = -14 \rightarrow 16$   
 $l = -16 \rightarrow 16$   
 Intensity decay: negligible

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.118$   
 $S = 1.02$   
 6632 reflections  
 317 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.3818P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.23$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

O1—C17	1.2283 (17)	O7—C110	1.2857 (17)
O2—C17	1.2761 (17)	O8—C110	1.2321 (17)
O3—C18	1.2926 (17)	N21—C22	1.4958 (19)
O4—C18	1.2286 (17)	N21—C26	1.4913 (18)
O5—C19	1.2184 (18)	N31—C32	1.4950 (19)
O6—C19	1.2958 (18)	N31—C36	1.4902 (18)
C12—C11—C17	128.03 (12)	C14—C15—C110	128.12 (12)
C16—C11—C17	114.19 (11)	C16—C15—C110	114.19 (11)
C11—C12—C18	128.15 (12)	O1—C17—O2	121.11 (13)
C13—C12—C18	114.06 (11)	O3—C18—O4	120.99 (13)
C13—C14—C19	113.87 (11)	O5—C19—O6	122.61 (13)
C15—C14—C19	128.02 (12)	O7—C110—O8	122.43 (13)
C16—C11—C17—O1	−12.92 (19)	C26—C25—C24—C4	175.31 (12)
C16—C11—C17—O2	166.49 (13)	C25—C24—C4—C5	171.36 (12)
C13—C12—C18—O3	−164.37 (13)	C24—C4—C5—C6	176.32 (12)
C13—C12—C18—O4	13.61 (19)	C4—C5—C6—C34	−175.44 (12)
C13—C14—C19—O5	20.4 (2)	C5—C6—C34—C33	171.36 (12)
C13—C14—C19—O6	−159.13 (13)	C6—C34—C35—C36	−177.21 (11)
C16—C15—C110—O7	160.19 (13)	C23—C24—C4—C5	−67.74 (17)
C16—C15—C110—O8	−18.25 (19)	C35—C34—C6—C5	−65.98 (16)

**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>
O3—H3...O2	1.20	1.20	2.395 (2)	175
O6—H7...O7	1.20	1.20	2.383 (2)	172
O9—H91...O6	0.89	2.09	2.980 (2)	175
O9—H92...O8 <sup>i</sup>	0.89	1.87	2.756 (2)	171
N21—H21A...O9	0.94	1.86	2.798 (2)	173
N21—H21B...O4 <sup>ii</sup>	0.94	2.02	2.933 (2)	164
N31—H31A...O1 <sup>iii</sup>	0.94	1.86	2.787 (2)	170
N31—H31B...O2 <sup>iv</sup>	0.94	2.37	3.204 (2)	148

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

All H atoms were clearly defined in difference maps and were then treated as riding atoms with C—H = 0.95–1.00 Å, N—H = 0.94 Å, water O—H = 0.89 Å (initially allowed to refine then restrained

to the refined value with a *DFIX* command) and carboxyl O—H = 1.20 Å (placed at the centre of each of the short O...H...O hydrogen bonds). Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

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: *NRCVAX96* (Gabe *et al.*, 1989) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2000); software used to prepare material for publication: *NRCVAX-96*, *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: GG1025). Services for accessing these data are described at the back of the journal.

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