

## Tetrakis(methylammonium) benzene-1,2,4,5-tetracarboxylate dihydrate

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In the title compound,  $4\text{CH}_6\text{N}^+\cdot\text{C}_{10}\text{H}_2\text{O}_8^{4-}\cdot 2\text{H}_2\text{O}$ , the complete  $\text{C}_{10}\text{H}_2\text{O}_8^{4-}$  anion is generated by inversion; one of the unique carboxylate groups is almost coplanar with the benzene ring, perhaps as the result of intramolecular  $\text{C}-\text{H}\cdots\text{O}$  interactions, and the other is almost perpendicular. A network of  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds helps to consolidate the crystal packing.

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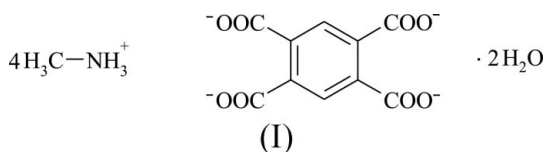
## Key indicators

Single-crystal X-ray study  
 $T = 298\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.032  
 $wR$  factor = 0.092  
Data-to-parameter ratio = 10.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

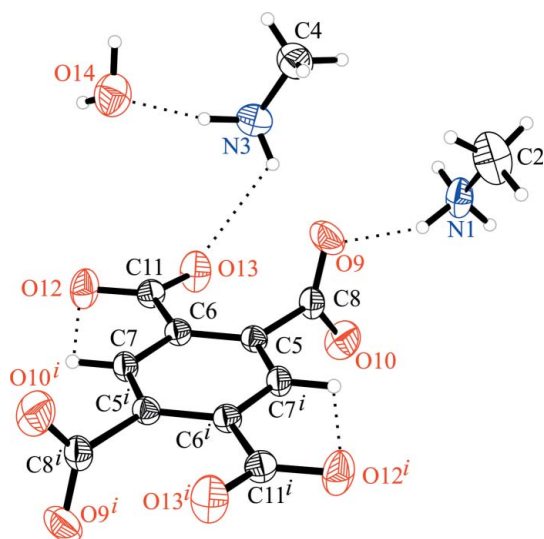
## Comment

Molecular design of new materials possessing interesting structures and properties is an important area in organic crystal engineering. A key aspect of this strategy is the consideration of intermolecular hydrogen bonds between molecules or ions in the crystal structure. Carboxylates have been intensively studied: supramolecular hydrogen-bonded assemblies of pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid) and its various anions with charges of  $-1$ ,  $-2$ ,  $-3$  and  $-4$  with ammonium (Bergstrom *et al.*, 2000), amines (Adams & Ramdas, 1979; Su *et al.*, 2001; Zhu *et al.*, 2002) and aromatic aza compounds (*e.g.* 1,10-phenanthroline, 1,7-phenanthroline, phenazine, derivatives of pyridine and 4,4'-bipyridinium) have been studied (Arora & Pedireddi, 2003; Ruiz-Perez *et al.*, 2004; Wang *et al.*, 2005).



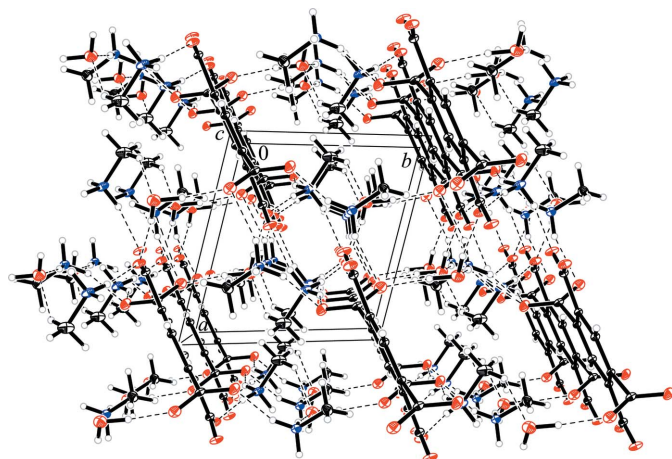
We report here the preparation and structural characterization of the title compound, (I), which is an organic salt of pyromellitic acid and methylamine. The crystal structure of (I) consists of methylammonium cations,  $\text{C}_{10}\text{H}_2\text{O}_8^{4-}$  pyromellitate(4 $-$ ) tetra-anions and water molecules (Fig. 1). It is notable that in all known alkylammonium or ammonium pyromellitates, water molecules of crystallization are present (Bergstrom *et al.*, 2000; Adams & Ramdas, 1979; Su *et al.*, 2001; Zhu *et al.*, 2002). The geometry of the two independent methylammonium cations in (I) are normal (*e.g.* Thomas, 1975).

The centrosymmetric pyromellitate(4 $-$ ) anion has one intramolecular  $\text{C}7-\text{H}7\cdots\text{O}12$  hydrogen bond forming a five-membered ring (Fig. 1). This bond may help to maintain the  $\text{C}11/\text{O}12/\text{O}13$  carboxylate group in an orientation almost coplanar with the benzene ring [dihedral angle =  $5.0(2)^\circ$ ]. Conversely, the  $\text{C}8/\text{O}9/\text{O}10$  carboxylate group is almost perpendicular to the ring plane [dihedral angle =  $82.52(5)^\circ$ ].



**Figure 1**

The structural components of (I). Hydrogen bonds are shown as dotted lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i)  $-x, -y, -z$ .]



**Figure 2**

The packing of (I), showing the intermolecular hydrogen-bonding scheme (dashed lines).

Otherwise, the geometrical parameters for the pyromellitate anion correlate well with the corresponding values found in related crystal structures (Arora & Pedireddi, 2003; Dale *et al.*, 2004; Sun *et al.*, 2002; Ruiz-Perez *et al.*, 2004; Zhu *et al.*, 2003). The two C—O bond lengths for each carboxylate group are almost identical (Table 1), indicating charge delocalization.

The crystal packing of (I) (Fig. 2) is stabilized by ionic interactions between the methylammonium cations and pyromellitate(4 $-$ ) anions, as well as by the network of O—H $\cdots$ O, N—H $\cdots$ O and C—H $\cdots$ O hydrogen bonds (Table 2).

## Experimental

Crystals of (I) were grown by slow evaporation of an aqueous solution containing methylamine and benzene-1,2,4,5-tetracarboxylic acid in a 4:1 stoichiometric ratio at room temperature.

## Crystal data

$4\text{CH}_6\text{N}^+\cdot\text{C}_{10}\text{H}_2\text{O}_8^{4-}\cdot 2\text{H}_2\text{O}$   
 $M_r = 414.42$   
 Triclinic,  $P\bar{1}$   
 $a = 7.9844$  (6) Å  
 $b = 8.1959$  (7) Å  
 $c = 9.1928$  (8) Å  
 $\alpha = 115.958$  (8) $^\circ$   
 $\beta = 96.233$  (6) $^\circ$   
 $\gamma = 99.896$  (7) $^\circ$

$V = 521.24$  (9) Å $^3$   
 $Z = 1$   
 $D_x = 1.320$  Mg m $^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm $^{-1}$   
 $T = 298$  (2) K  
 Block, colourless  
 $0.50 \times 0.48 \times 0.45$  mm

## Data collection

Oxford Diffraction Xcalibur diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 3377 measured reflections

1915 independent reflections  
 1673 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.016$   
 $\theta_{\text{max}} = 25.5^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.092$   
 $S = 1.05$   
 1915 reflections  
 188 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.0982P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.20$  e Å $^{-3}$   
 $\Delta\rho_{\text{min}} = -0.15$  e Å $^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.168 (13)

**Table 1**

Selected bond lengths (Å).

C8—O10	1.246 (2)	C11—O13	1.247 (1)
C8—O9	1.250 (2)	C11—O12	1.256 (1)

**Table 2**

Hydrogen-bond geometry (Å,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ O9	0.94 (2)	1.98 (2)	2.828 (2)	149 (2)
N1—H1B $\cdots$ O12 $^i$	0.92 (2)	1.90 (2)	2.813 (2)	172 (2)
N1—H1C $\cdots$ O13 $^{ii}$	0.93 (2)	1.89 (2)	2.794 (2)	164 (2)
N3—H3A $\cdots$ O9	0.93 (2)	1.92 (2)	2.809 (2)	160 (2)
N3—H3B $\cdots$ O10 $^{ii}$	0.92 (2)	2.00 (2)	2.869 (2)	159 (2)
N3—H3C $\cdots$ O14	0.98 (2)	1.80 (2)	2.762 (2)	167 (2)
O14—H14A $\cdots$ O12 $^{iii}$	0.86 (3)	1.91 (3)	2.758 (2)	173 (2)
O14—H14B $\cdots$ O10 $^{iv}$	0.98 (3)	1.77 (3)	2.736 (2)	166 (2)
C2—H2B $\cdots$ O14 $^i$	0.98 (3)	2.43 (3)	3.305 (2)	149 (2)
C7—H7 $\cdots$ O12	0.96 (1)	2.43 (1)	2.770 (1)	100.5 (9)

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

The H atoms were located in difference maps and their positions and  $U_{\text{iso}}$  values were freely refined [ $C-H = 0.93$  (3)– $1.01$  (2) Å].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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