

## Hydrogen-bonded bilayers in piperazinium(2+) bis(mandelate) bis(methanol) solvate

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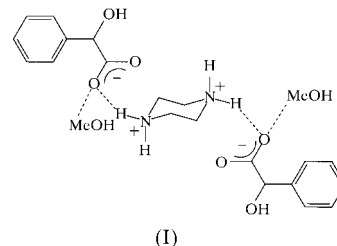
In the title compound,  $C_4H_{12}N_2^{2+} \cdot 2C_8H_7O_3^- \cdot 2CH_4O$ , the cations lie across centres of inversion and are disordered over two orientations with equal occupancy; there are equal numbers of (*R*)- and (*S*)-mandelate anions present (mandelate is  $\alpha$ -hydroxybenzeneacetate). The anions and the neutral water molecules are linked by O—H...O hydrogen bonds [ $O \cdots O$  2.658 (3) and 2.682 (3) Å, and O—H...O 176 and 166°] into deeply folded zigzag chains. Each orientation of the cation forms two symmetry-related two-centre N—H...O hydrogen bonds [ $N \cdots O$  2.588 (4) and 2.678 (4) Å, and N—H...O 177 and 171°] and two asymmetric, but planar, three-centre N—H...O hydrogen bonds [ $N \cdots O$  2.686 (4)–3.137 (4) Å and N—H...O 137–147°], and by means of these the cations link the anion/water chains into bilayers.

### Comment

We have recently described the supramolecular structures of some adducts formed between diamines and aromatic carboxylic acids carrying hydrogen-bonding functional groups on the aryl rings (Burchell *et al.*, 2000; Burchell, Ferguson *et al.*, 2001; Burchell, Glidewell *et al.*, 2001). Developing this study to include acids where the additional functionality is distinct from the aryl ring, we have now characterized the 1:2 adduct formed between piperazine and racemic mandelic acid [2-hydroxy-2-phenylacetic acid,  $PhCH(OH)COOH$ ], which crystallizes from methanol as the title solvated salt,  $[H_2N(CH_2CH_2)_2NH_2]^{2+} \cdot 2[PhCH(OH)COO]^- \cdot 2MeOH$ , (I). The structures of several mandelate salts of diamines have been reported previously, but in all cases a single enantiomer of the acid was employed, as the emphasis was primarily on establishing the absolute configuration of the diamine

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component (De Costa *et al.*, 1989; Acs *et al.*, 1992; Larsen *et al.*, 1993; Gjerløv & Larsen, 1997*a,b*; Barnes & Weakley, 1998). By contrast, the diamine component in compound (I) is achiral, the acid is a racemic mixture of enantiomers and the primary emphasis is on the supramolecular structure.



(I)

In compound (I), the cation lies across a centre of inversion, chosen for convenience as that at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , while the anion and the neutral methanol molecule lie in general positions. In space group *Pbca*, there are thus four cations per unit cell and equal numbers of (*R*)- and (*S*)-mandelate anions. The cations are disordered, with two orientations having equal occupancy; in both orientations, the ring adopts the usual chair conformation such that the two sets of C-atom positions are virtually coincident (Fig. 1). Each cation, of whichever orientation, acts as a fourfold donor in N—H...O hydrogen bonds, and each anion accepts such bonds from two different cations. The methanol molecule acts as both a single donor and a single acceptor of O—H...O hydrogen bonds. The three components are linked into two-dimensional sheets, which are most simply analysed in terms of the one-dimensional chains formed by the anions and the methanol molecules, and of the linking of these chains by the disordered cations.

Within the asymmetric unit, methanol atom O4 acts as a hydrogen-bond donor to carboxylate atom O1 (Fig. 1) and hydroxyl atom O3 at  $(x, y, z)$  acts as a donor to methanol atom O4 at  $(\frac{1}{2} - x, y - \frac{1}{2}, z)$ , while atom O3 at  $(\frac{1}{2} - x, y - \frac{1}{2}, z)$  acts as a donor to O4 at  $(x, y - 1, z)$ . Hence, these two hydrogen bonds produce a  $C_2^2(7)$  chain running parallel to [010] and

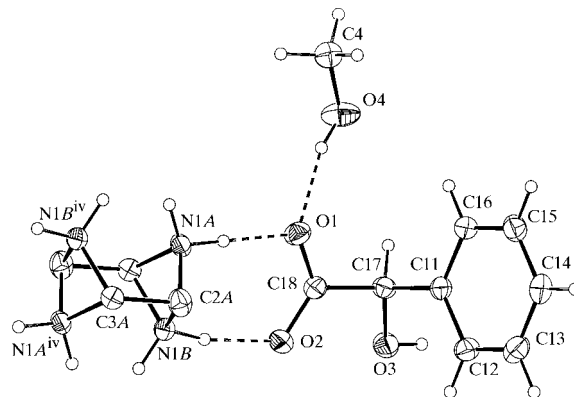
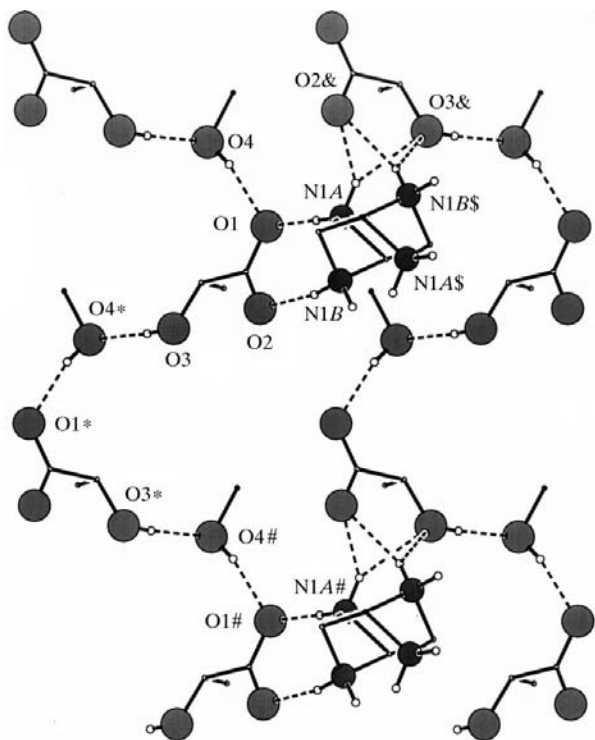


Figure 1

The molecular components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and the alternative sites N1A and N1B each have 50% occupancy [symmetry code: (iv)  $1 - x, 1 - y, 1 - z$ ]. The 50% occupancy sites C2A/C2B and C3A/C3B are almost coincident and the H atoms bonded to these disordered C atoms have been omitted for the sake of clarity.

generated by the glide plane at  $x = \frac{5}{4}$ . There are four of these zigzag chains passing through each unit cell, and each chain contains both enantiomers of the anion. The reference chain lies in the domain  $0.54 < z < 0.74$ , and the other three chains lie in the domains  $0.04 < z < 0.24$ ,  $0.26 < z < 0.46$  and  $0.76 < z < 0.96$ . Within each domain, parallel chains are linked by the cations into sheets, and pairs of these sheets related by centres of inversion are likewise linked into bilayers; there are, however, no significant interactions between adjacent bilayers.

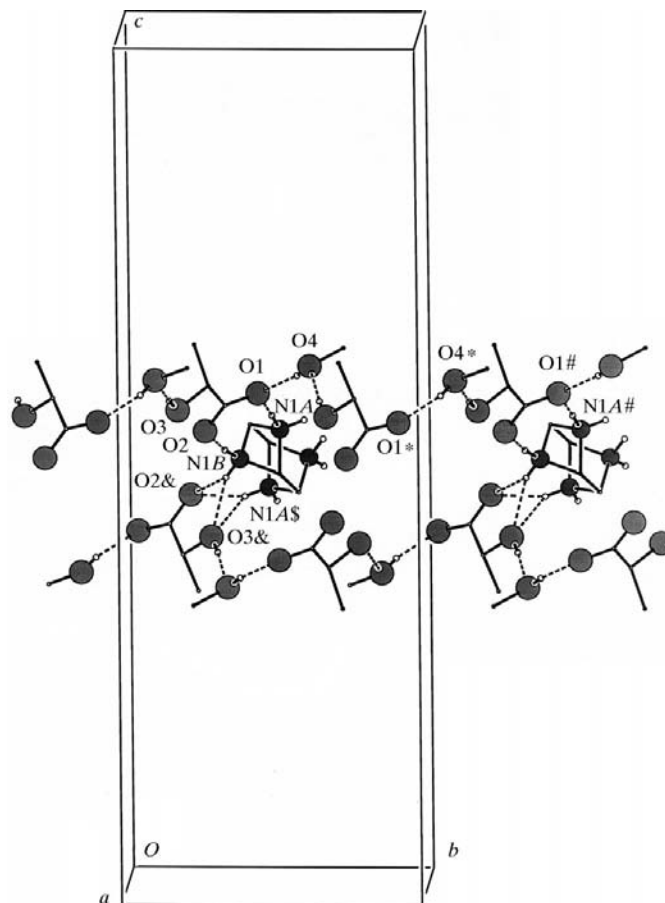
Each N atom, regardless of the orientation of the cation in which it lies, forms a two-centre hydrogen bond to a carboxylate O atom, O1 in the case of N1A and O2 in the case of N1B, both within the asymmetric unit, and also a planar three-centre hydrogen bond to carboxylate atom O2 and hydroxyl atom O3, both of which are at  $(\frac{3}{2} - x, \frac{1}{2} + y, z)$  in the case of N1A and at  $(x - \frac{1}{2}, \frac{1}{2} - y, 1 - z)$  in the case of N1B



**Figure 2**  
Part of the structure of (I) showing the linking of [010] chains into a (001) sheet. For the sake of clarity, H atoms bonded to C atoms and to atoms C12 and C16 of the anion have been omitted. Atoms marked with an asterisk (\*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions  $(\frac{3}{2} - x, -\frac{1}{2} + y, z)$ ,  $(x, -1 + y, z)$ ,  $(1 - x, 1 - y, 1 - z)$  and  $(\frac{3}{2} - x, \frac{1}{2} + y, z)$ , respectively.

(Table 1). For the cation orientation defined by N1A, the N atom at  $(x, y, z)$  in the cation centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  forms N—H...O hydrogen bonds to three acceptors, all in the domain  $0.54 < z < 0.74$ , while the symmetry-related N atom in the same cation, which is at  $(1 - x, 1 - y, 1 - z)$ , forms hydrogen bonds to acceptors in the domain  $0.26 < z < 0.46$ . In these cations, the hydrogen bonds formed by each individual N atom link  $C_2^2(7)$  chains into an (001) sheet (Fig. 2), while those formed by the cation as a whole link pairs of (001) sheets related by centres of inversion, forming a bilayer (Fig. 3).

The cation whose orientation is defined by N1B exhibits a different pattern of hydrogen bonds: N1B at  $(x, y, z)$  forms a two-centre hydrogen bond to an acceptor in the domain  $0.54 < z < 0.74$  and a three-centre hydrogen bond to an acceptor in the domain  $0.26 < z < 0.46$ , while this pattern is reversed for the symmetry-related N1B at  $(1 - x, 1 - y, 1 - z)$ . In this type



**Figure 3**  
Part of the structure of (I) showing the linking of adjacent (001) sheets into a bilayer. For the sake of clarity, H atoms bonded to C atoms and to atoms C12 and C16 of the anion have been omitted. Atoms marked with an asterisk (\*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions  $(\frac{3}{2} - x, \frac{1}{2} + y, z)$ ,  $(x, 1 + y, z)$ ,  $(1 - x, 1 - y, 1 - z)$  and  $(-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ , respectively.

of cation, the hydrogen bonds formed by N1B—H1B at  $(x, y, z)$  and by N1B—H2B at  $(1 - x, 1 - y, 1 - z)$  link  $C_2^2(7)$  chains into (001) sheets (Fig. 2), while again the entire cations link pairs of sheets into bilayers (Fig. 3).

## Experimental

Stoichiometric quantities of piperazine and racemic mandelic acid were separately dissolved in methanol. The solutions were mixed and the mixture was set aside to crystallize, producing analytically pure (I). Analysis, found: C 58.8, H 7.7, N 6.4%;  $C_{22}H_{34}N_2O_8$  requires: C 58.1, H 7.5, N 6.2%. Crystals of (I) suitable for single-crystal X-ray diffraction were selected from the analytical sample.

## Crystal data

$C_4H_{12}N_2^{2+} \cdot 2C_8H_7O_3^- \cdot 2CH_4O$   
 $M_r = 454.51$   
 Orthorhombic, *Pbca*  
 $a = 7.7360$  (2) Å  
 $b = 10.2394$  (4) Å  
 $c = 29.7822$  (11) Å  
 $V = 2359.11$  (14) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.280$  Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 2290 reflections  
 $\theta = 2.7$ – $25.0^\circ$   
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Needle, colourless  
 $0.28 \times 0.16 \times 0.12$  mm

## Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  scans, and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)  
 $T_{\min} = 0.973$ ,  $T_{\max} = 0.988$   
 11 737 measured reflections

2074 independent reflections  
 1077 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.089$   
 $\theta_{\max} = 25^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -12 \rightarrow 12$   
 $l = -35 \rightarrow 35$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.133$   
 $S = 0.91$   
 2074 reflections  
 163 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0694P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.19$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.22$  e Å<sup>-3</sup>

Table 1

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>
N1A—H2A...O1	0.92	1.67	2.588 (4)	177
N1A—H1A...O2 <sup>i</sup>	0.92	1.88	2.686 (4)	144
N1A—H1A...O3 <sup>i</sup>	0.92	2.37	3.137 (4)	141
N1B—H1B...O2	0.92	1.77	2.678 (4)	171
N1B—H2B...O3 <sup>ii</sup>	0.92	2.09	2.841 (4)	137
N1B—H2B...O2 <sup>ii</sup>	0.92	2.15	2.967 (4)	147
O3—H3...O4 <sup>iii</sup>	0.84	1.82	2.658 (3)	176
O4—H31...O1	0.84	1.86	2.682 (3)	166

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

At an early stage in the analysis, it became clear that the N atoms of the centrosymmetric cation were disordered over two sites. Refinement of the site-occupancy factors (s.o.f.'s) for the two sites,

denoted N1A and N1B, led to values not significantly different from 0.5. Hence, the s.o.f.'s were fixed at 0.5 in the final refinements. H atoms were treated as riding, with distances C—H = 0.95–1.00, N—H = 0.92 and O—H = 0.84 Å.

Data collection: *COLLECT* (Nonius, 1997–2000); 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, 2001); software used to prepare material for publication: *SHELXL97* and *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: SK1483). Services for accessing these data are described at the back of the journal.

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