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Two salts of di-*p*-toluoyltartaric acid with aromatic amines

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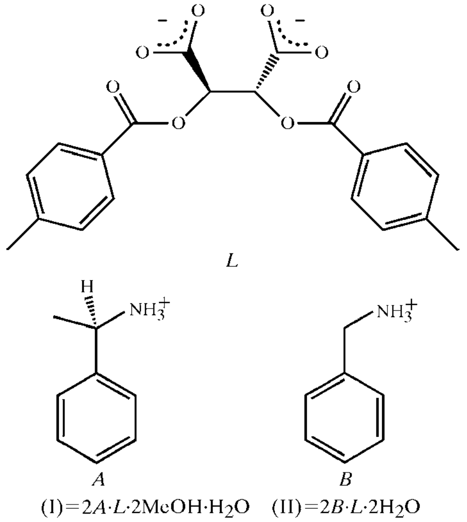
The structures of bis[(*R*)-(+)-1-phenylethylammonium] (2*R*,3*R*)-(−)-2,3-di-*p*-toluoyloxybutanedioate methanol disolvate monohydrate, $2C_8H_{12}N^+\cdot C_{20}H_{16}O_8^{2-}\cdot 2CH_4O\cdot H_2O$, (I), and bis(benzylammonium) (2*R*,3*R*)-(−)-2,3-di-*p*-toluoyloxybutanedioate dihydrate, $2C_7H_{10}N^+\cdot C_{20}H_{16}O_8^{2-}\cdot 2H_2O$, (II), exhibit extensive hydrogen bonding, with (N—)H···O and (O—)H···O distances in the ranges 2.716 (2)–2.929 (3) and 2.687 (2)–2.767 (2) Å, respectively, in (I), and 2.673 (2)–2.888 (2) and 2.785 (2)–2.931 (2) Å, respectively, in (II). The amine groups are protonated and the carboxylate groups of the tartrate anions are fully deprotonated. The conformation of the toluoyltartrate anion and its molecular parameters are similar in both structures.

Comment

This work arose from a systematic study of chiral host acids with amine guests. Previous examples of the structures derived from the host (2*R*,3*R*)-(−)-di-*O*-*p*-toluoyltartaric acid or its enantiomer with amines showed that the acid is mono-deprotonated (Liao *et al.*, 2003; Hansen *et al.*, 1998). Liao *et al.* (2003) have characterized the structure of (*R*)-α-{[(1,1-dimethylethyl)ammonio]methyl}(3,5-dihydroxyphenyl)methanol (2*S*,3*S*)-di-*O*-toluoyltartrate monohydrate, in which the N atom on the base is protonated and one of the carboxylic acid moieties is deprotonated. The anhydrous salt of the same



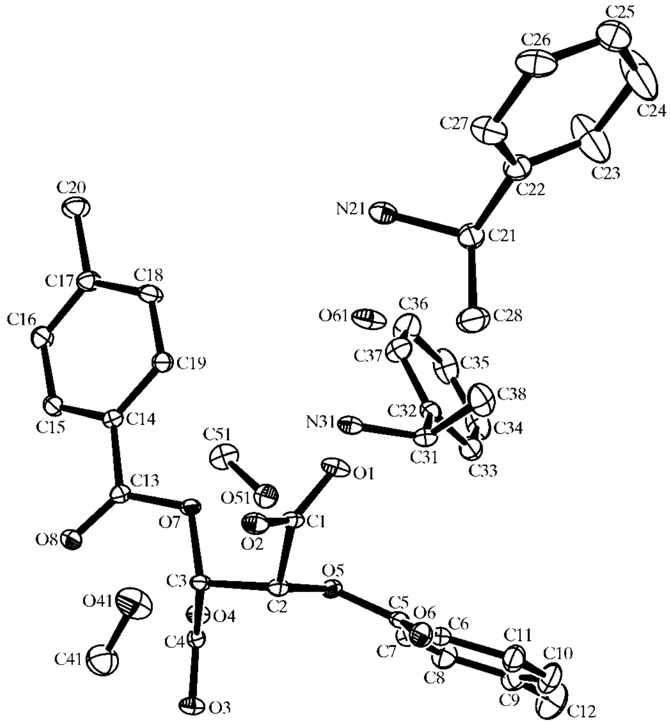


Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

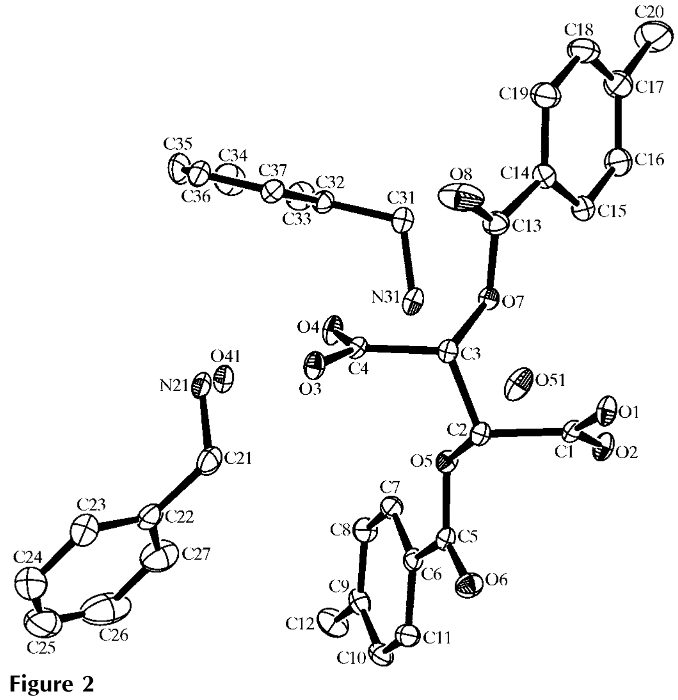


Figure 2
A view of the asymmetric unit of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

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compound has similar features [Cambridge Structural Database (CSD; Allen, 2002) refcodes GACXUE and GACYEP01, respectively]. Hansen *et al.* (1998) have described the structure of (+)-(*R*)-3-(*N*,*N*-dimethylammonio)-1,1-diphenyl-1-butanol (−)-(2*R*,3*R*)-*O*,*O*′-di-*p*-toloyltartrate, in which the base is again protonated on the N atom and one carboxylic acid moiety is anionic (CSD refcode GORCAR). In contrast, the structure of (2*S*,5*S*)-1,6-diammonio-2,5-dimethyl-3,4-dithiahexane (2*S*,3*S*)-di-*O*-(4-toluoyl)tartrate ethanol solvate sesquihydrate (Elz *et al.*, 1987) shows the thiahexane to be bisprotonated and the tartrate to have lost two H atoms (CSD refcode FEWLEY). We noted these features by observing the C—O bond lengths of the carboxylic acid moieties in which there was no ambiguity as to whether the carboxylic acid moiety was deprotonated or not. In addition, the corresponding amines displayed an extra H atom at the N atom, the geometry of which was tetrahedral. We have also analysed differences in the conformations of the tartrate anions and have noted that the absolute value of the torsion angle about the central C—C bond is approximately 76° in the completely deprotonated anion, but is reduced to 61–70° in the monoprotonated species. There were no discernible patterns in the other four torsion angles in the adjacent C—O and O—C bonds of the tartrates, which are described later.

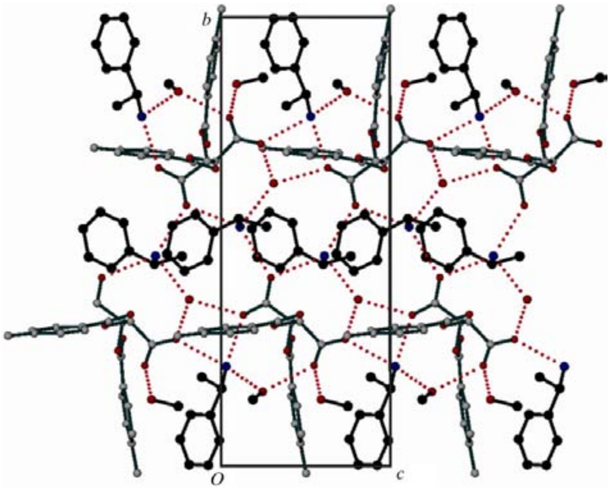

Figure 3
A projection of the structure of (I), viewed along [100], showing the network of hydrogen bonding. Various shading is used for different molecules and bonds, and hydrogen bonds are shown as dotted lines. All H atoms have been omitted for clarity.

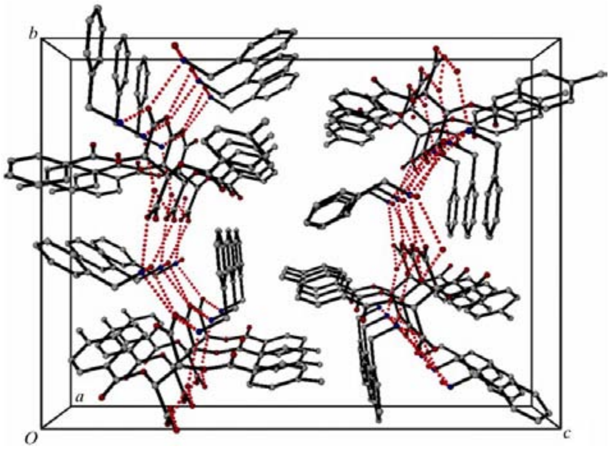

Figure 4
A perspective view of (II), along [100], showing the infinite sheets of the hydrogen-bonding network running perpendicular to [001]. Hydrogen bonds are shown as dotted lines. All H atoms have been omitted for clarity.

We have characterized the structures of (2*R*,3*R*)-2,3-di-*p*-toluoyltartrate, *L*, with (*R*)-(+)-1-phenylethylammonium (*A*) and benzylammonium (*B*) (see scheme), and present the results here. The former forms a compound with the stoichiometry $L\cdot 2A\cdot 2\mathrm{MeOH}\cdot\mathrm{H_2O}$ [compound (I); Fig. 1] and the latter a compound with the stoichiometry $L\cdot 2B\cdot 2\mathrm{H_2O}$ [compound (II); Fig. 2].

Compound (I) crystallizes in the space group $P2_1$ with $Z = 2$. The refinement showed that the N atoms of the amines are protonated and the carboxyl moieties of the acid exhibit similar C—O bond lengths, ranging from 1.240 (3) to 1.257 (3) Å, so they may be represented as $(\mathrm{CO_2})^-$ moieties.

The structure is extensively hydrogen bonded, as shown in Fig. 3. There are double ribbons of the toluoyltartrate anions running in the [010] direction, which are bridged by 1-phenylethylammonium cations and water molecules, while the methanol molecules are hydrogen bonded to the ammonium and carboxylate groups. Details of the hydrogen bonding are given in Table 2.

The conformation of the toluoyltartrate anion is governed by the torsion angles about the central C—C bond and the adjacent C—O and O—C bonds. These are reported in Table 1, together with salient bond lengths. The conformation is such that the aromatic toluoyl moieties lie approximately perpendicular to each other.

Compound (II) crystallizes in the space group $P2_12_12_1$ with $Z = 4$. The toluoyltartaric acid again forms anions, with both its carboxyl moieties deprotonated, and the amines display protonated N atoms. The packing is such that the structure forms infinite sheets perpendicular to [001] held together by hydrogen bonds in which the water molecules and amine cations bridge the acid anions. This is shown in Fig. 4. Details of the hydrogen bonding are given in Table 4. The conformation of the toluoyltartrate in this structure is similar to that of (I), as are the C—O bond lengths of the carboxylate moiety (Table 3).

We note that the absolute values of the torsion angles about the central C—C bond of the anions in these compounds are close to that found in the dithiahexane compound elucidated by Elz *et al.* (1987).

Experimental

Tartaric acid and the appropriate amine guest, in a molar ratio of 1:2, were dissolved in warm wet methanol solvent at 323 K, using 95% methanol for both compounds. The resultant solutions were allowed to stand at room temperature. Colourless crystals of (I) and (II) appeared after a few days from their respective mother liquors.

Salt (I)

Crystal data

$2C_8H_{12}N^+ \cdot C_{20}H_{16}O_8^{2-} \cdot 2CH_4O \cdot H_2O$
$M_r = 710.80$
Monoclinic, $P2_1$
$a = 10.9366\ (1)$ Å
$b = 8.0785\ (1)$ Å
$c = 22.0995\ (2)$ Å
$\beta = 103.324\ (1)°$
$V = 1899.96\ (3)$ Å^3
$Z = 2$
$D_x = 1.242$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 113\ (2)$ K
Prism, colourless
$0.40 \times 0.40 \times 0.35$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
1.2° φ scans and ω scans
7708 measured reflections
7708 independent reflections
3969 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.009$
$\theta_{\rm max} = 26.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.095$
$S = 1.12$
7708 reflections
502 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.6269P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.035 (3)

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C1	1.251 (3)	O7—C3	1.437 (2)
O2—C1	1.251 (3)	C1—C2	1.537 (3)
O3—C4	1.257 (3)	C2—C3	1.520 (3)
O4—C4	1.240 (3)	C3—C4	1.547 (3)
O5—C2	1.445 (2)		
C5—O5—C2—C3	−156.8 (2)	C2—O5—C5—C6	165.5 (2)
C13—O7—C3—C2	−171.0 (2)	C3—O7—C13—C14	−178.0 (2)
O5—C2—C3—O7	−76.3 (2)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O61	0.95 (3)	1.80 (2)	2.716 (3)	158 (3)
N21—H21B···O2$^{\rm i}$	0.96 (1)	1.99 (1)	2.929 (3)	166 (3)
N21—H21C···O2$^{\rm ii}$	0.95 (1)	1.95 (2)	2.846 (3)	155 (3)
N31—H31A···O3$^{\rm i}$	0.95 (3)	1.87 (1)	2.795 (3)	162 (3)
N31—H31B···O51	0.96 (1)	1.82 (1)	2.768 (3)	170 (3)
N31—H31C···O1	0.95 (3)	1.92 (1)	2.843 (2)	165 (3)
O41—H41···O4	1.00 (4)	1.82 (2)	2.767 (3)	158 (5)
O51—H51···O4	0.99 (3)	1.82 (2)	2.757 (3)	158 (3)
O61—H61A···O3$^{\rm i}$	0.94 (3)	1.81 (3)	2.750 (2)	172 (4)
O61—H61B···O1	0.94 (1)	1.80 (2)	2.687 (2)	156 (4)

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

Salt (II)

Crystal data

$2C_7H_{10}N^+ \cdot C_{20}H_{16}O_8^{2-} \cdot 2H_2O$
$M_r = 636.68$
Orthorhombic, $P2_12_12_1$
$a = 6.8805\ (1)$ Å
$b = 19.2606\ (1)$ Å
$c = 25.5545\ (2)$ Å
$V = 3386.55\ (6)$ Å^3
$Z = 4$
$D_x = 1.249$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 113\ (2)$ K
Prism, colourless
$0.35 \times 0.25 \times 0.25$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
1.2° φ scans and ω scans
28533 measured reflections
4225 independent reflections
3955 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\rm max} = 27.2°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.084$
$S = 1.07$
4225 reflections
458 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.6428P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.017 (2)

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C1	1.259 (2)	O7—C3	1.446 (2)
O2—C1	1.237 (2)	C1—C2	1.545 (2)
O3—C4	1.253 (2)	C2—C3	1.516 (2)
O4—C4	1.249 (2)	C3—C4	1.545 (2)
O5—C2	1.438 (2)		
C5—O5—C2—C3	−156.6 (1)	C2—O5—C5—C6	−179.4 (1)
C13—O7—C3—C2	−151.0 (1)	C3—O7—C13—C14	173.4 (1)
O5—C2—C3—O7	−76.5 (1)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21A···O41$^{\rm i}$	0.96 (1)	1.93 (1)	2.875 (2)	169 (2)
N21—H21B···O4	0.95 (1)	2.02 (1)	2.888 (2)	150 (2)
N21—H21C···O1$^{\rm ii}$	0.96 (1)	1.72 (1)	2.673 (2)	172 (2)
N31—H31A···O3$^{\rm i}$	0.95 (1)	1.87 (1)	2.803 (2)	168 (2)
N31—H31B···O51	0.95 (1)	1.93 (1)	2.807 (2)	153 (2)
N31—H31C···O4	0.96 (1)	1.79 (1)	2.729 (2)	168 (2)
O41—H41A···O3	0.94 (1)	1.88 (1)	2.785 (2)	160 (2)
O41—H41B···O2$^{\rm ii}$	0.94 (3)	2.00 (3)	2.931 (2)	173 (3)
O51—H51A···O1$^{\rm i}$	0.94 (1)	1.86 (1)	2.783 (2)	168 (2)
O51—H51B···O2	0.94 (1)	1.90 (1)	2.804 (2)	162 (2)

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

Both structure solutions and refinements proceeded routinely. Friedel equivalents were merged in the final refinement cycles. The functional H atoms of the methanol hydroxyl group, the water hydroxyl group and the amine NH_3^+ cation were located in a difference electron-density map and refined independently with simple bond-length restraints: methanol O—H = 0.99 (1) Å, water O—H = 0.95 (1) Å and N—H = 0.96 (1) Å. The remaining H atoms were placed in idealized positions in a riding model, with C—H = 0.95–1.00 Å, and refined with $U_{\rm iso}({\rm H}) = 1.2$–$1.5U_{\rm eq}({\rm C})$.

For both salts, data collection: *COLLECT* (Nonius, 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: *ORTEP-3* (Farrugia, 1997), *X-SEED* (Barbour, 2001) and *POVRAY* (Persistance of Vision Development Team, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1300). Services for accessing these data are described at the back of the journal.

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