

**(*R*)-1-Phenylethanaminium–(*S,S*)-2,3-dibromo-succinate–(*R,R*)-2,3-dibromosuccinic acid–water (2/1/1/2)****Andreas Fischer**Inorganic Chemistry, School of Chemical  
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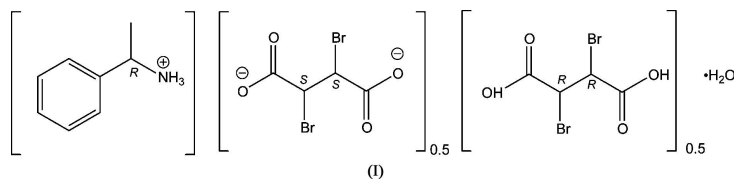
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**Key indicators**Single-crystal X-ray study  
 $T = 299$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.013$  Å  
 $R$  factor = 0.059  
 $wR$  factor = 0.120  
Data-to-parameter ratio = 20.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

From an aqueous solution of racemic 2,3-dibromosuccinic acid and (*R*)-1-phenylethanamine, crystals of the title compound,  $\text{C}_8\text{H}_{12}\text{N}^+ \cdot 0.5\text{C}_4\text{H}_2\text{Br}_2\text{O}_4^{2-} \cdot 0.5\text{C}_4\text{H}_4\text{Br}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , were obtained in almost quantitative yield. The structure contains both enantiomers of the starting material, dibromosuccinic acid. The *S,S* enantiomer is present as a dianion and the *R,R* enantiomer as the neutral acid; both of these components lie on twofold rotation axes. The structure features a complex two-dimensional network of hydrogen bonds.

Received 15 February 2006  
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Recently, we reported the crystal structure of (*2R,3S*)-2,3-dibromosuccinic acid (dbs) (Eriksson *et al.*, 2006). The structure of racemic 2,3-dibromosuccinic acid had been reported earlier (Bolte & Degen, 2000). To determine the structure of the pure enantiomer, (*R,R*)- or (*S,S*)-dibromosuccinic acid, we tried to crystallize the dibromosuccinate with the enantiomerically pure base (*R*)-1-phenylethanamine. The result of this crystallization was, however, the title compound, (I), which is almost insoluble in water and whose structure is described here.



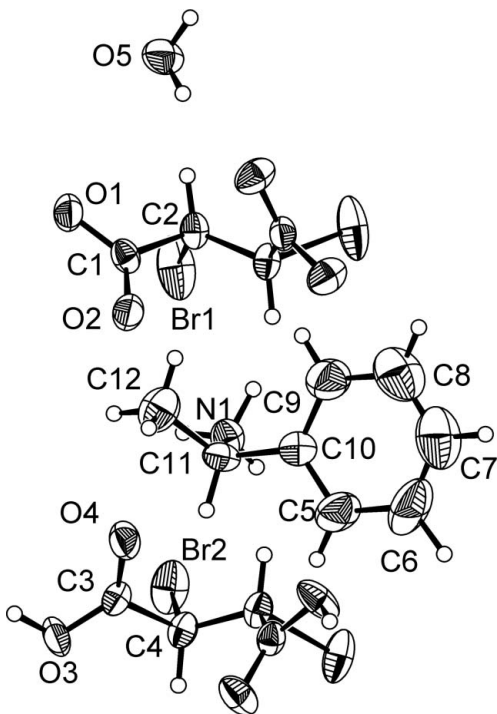
Compound (I) features phenylethanaminium cations, anions of the *2S,3S* enantiomer of dbs, the *2R,3R* enantiomer of the neutral  $\text{H}_2\text{dbs}$ , and water of crystallization. In both the anion and the neutral acid, a twofold rotation axis passes through the mid-point of the central C–C bond (Fig. 1 and Fig. 2). The bond lengths and angles in (I) are unexceptional.

The molecule of water of crystallization participates in hydrogen bonding, both as donor and acceptor. The hydrogen-bonding pattern is shown in Fig. 3, with numeric details in Table 1.

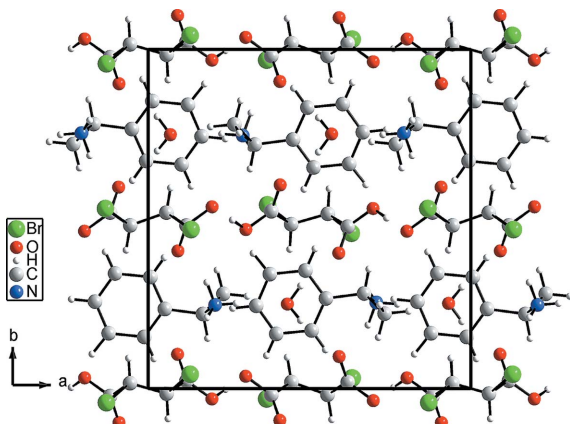
A similar crystallization behaviour has been reported recently (Li *et al.*, 2005) in the structure of the hydroxy-quinolinium salt of the *meso* form of dibromosuccinic acid, where both the protonated and deprotonated forms of dibromosuccinic acid are present.

**Experimental**

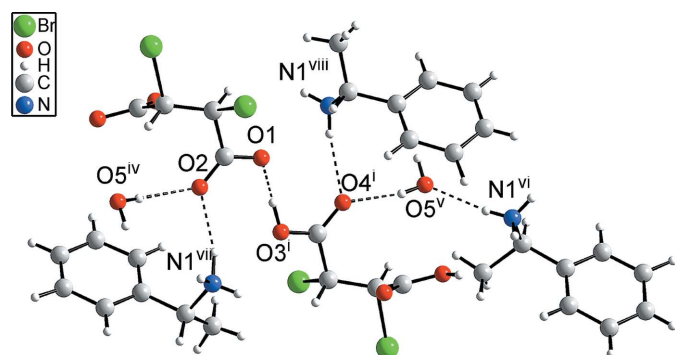
Racemic 2,3-dibromosuccinic acid was prepared from maleic acid and bromine. Maleic acid (8.35 g, Lancaster, 98%) was stirred in diethyl


**Figure 1**

The four components of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms in the anion are related to labelled atoms by  $(-x, 1 - y, z)$ . Unlabelled atoms in the acid are related to labelled atoms by  $(-x, -y, z)$ .


**Figure 2**

The unit-cell contents of (I), viewed along  $c$ .


**Figure 3**

The hydrogen-bonding (dashed lines) pattern in (I). Symmetry codes as in Table 1, plus (v)  $\frac{1}{2} - x, \frac{3}{2} - y, -z$ ; (vi)  $1 - x, 1 - y, -1 + z$ ; (vii)  $x, y, -1 + z$ ; (viii)  $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$ .

ether (100 ml) and bromine (12.1 g, Aldrich, 99.5%) was added. After complete dissolution of the maleic acid, the solution was evaporated and the residue was recrystallized from water. The yield after recrystallization was 13.3 g (67%). The racemate (276 mg) was dissolved in water (5 ml). Upon addition of (*R*)-1-phenylethylamine (0.13 ml, Fluka, purum, enantiomeric purity verified by measuring the optical rotation), the solution was kept at 323 K for 12 h. After this time, the title compound had crystallized in almost quantitative yield as crystals of up to several mm in size.

#### Crystal data

$C_8H_{12}N^+ \cdot 0.5C_4H_2Br_2O_4^{2-} \cdot 0.5C_4H_4Br_2O_4 \cdot H_2O$   
 $M_r = 415.07$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 12.609$  (2) Å  
 $b = 13.235$  (3) Å  
 $c = 9.689$  (2) Å  
 $V = 1616.8$  (6) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.705$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 39 reflections  
 $\theta = 8.0$ – $20.2^\circ$   
 $\mu = 5.03$  mm<sup>-1</sup>  
 $T = 299$  K  
 Fragment, colourless  
 $0.40 \times 0.30 \times 0.14$  mm

#### Data collection

Bruker–Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: numerical (*HABITUS*; Herrendorf & Bärnighausen, 1997)  
 $T_{min} = 0.265, T_{max} = 0.759$   
 12294 measured reflections

3652 independent reflections  
 2529 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.075$   
 $\theta_{max} = 27.5^\circ$   
 $h = -16 \rightarrow 15$   
 $k = -16 \rightarrow 17$   
 $l = -11 \rightarrow 12$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.059$   
 $wR(F^2) = 0.120$   
 $S = 1.21$   
 3652 reflections  
 181 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0061P)^2 + 4.8215P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.65$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.60$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1550 Friedel pairs  
 Flack parameter: 0.00 (3)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H3 \cdots O1^i$	0.95	1.48	2.431 (6)	177
$N1-H1A \cdots O5^{ii}$	0.83	2.01	2.828 (6)	172
$N1-H1B \cdots O2^{iii}$	0.99	2.02	2.947 (8)	155
$N1-H1C \cdots O4^{iii}$	0.85	2.12	2.948 (8)	164
$O5-H5A \cdots O4^{iv}$	0.88	1.97	2.833 (8)	167
$O5-H5B \cdots O2^{iv}$	0.86	2.07	2.910 (8)	165

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

The H atoms were located in a difference Fourier map and were refined in their as-found positions, using a riding model, with  $U_{iso}(H) = 1.2U_{eq}$  of the carrier atom, with C–H = 0.93–0.98 Å, N–H = 0.83–0.99 Å, water O–H = 0.86–0.88 Å and carboxyl O–H = 0.95 Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD* (Duisenberg, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1999).

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