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(*R*)-Methioninium–(*R*)-mandelate–(*R*)-mandelic acid (1/1/2)

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The title molecular complex, $C_5H_{12}NO_2S^+\cdot C_8H_7O_3^-\cdot 2C_8H_8O_3$, contains (*R*)-methioninium cations, (*R*)-mandelate anions and (*R*)-mandelic acid molecules. The (*R*)-methioninium cation assumes an *anti* conformation for all of its single bonds. Hydrophilic and hydrophobic layers alternate in the crystal structure. Hydrogen-bond interactions and van der Waals contacts occur in the hydrophilic and hydrophobic layers, respectively.

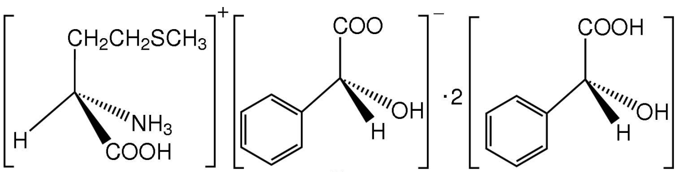
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.015 Å
R factor = 0.086
wR factor = 0.250
Data-to-parameter ratio = 7.8

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

Comment

During investigations on separating a racemic mixture into its enantiomers through formation of a diastereomeric molecular complex by reaction with an optically active compound in our laboratory (Hu *et al.*, 2001), the title molecular complex, (I) (Fig. 1), has been prepared and its crystal structure is presented here.



(I)

The crystal structure of (I) consists of (*R*)-methioninium cations, (*R*)-mandelate anions and (*R*)-mandelic acid molecules. The absolute configuration of (I) was established on the basis of the known configuration of the starting reagent

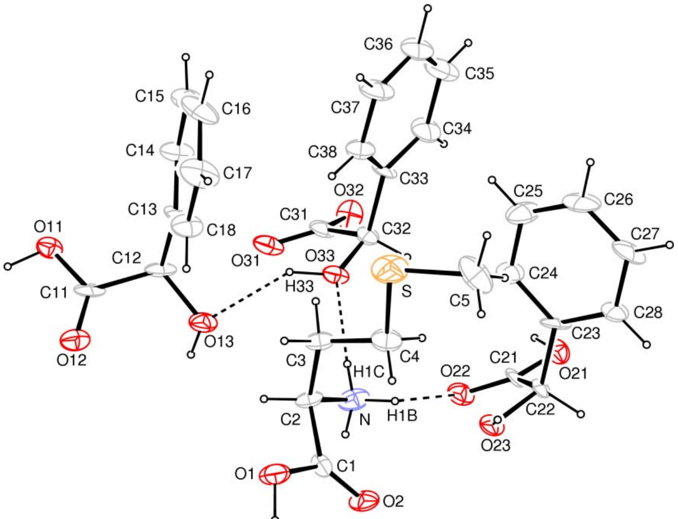


Figure 1
The asymmetric unit of (I), with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding.

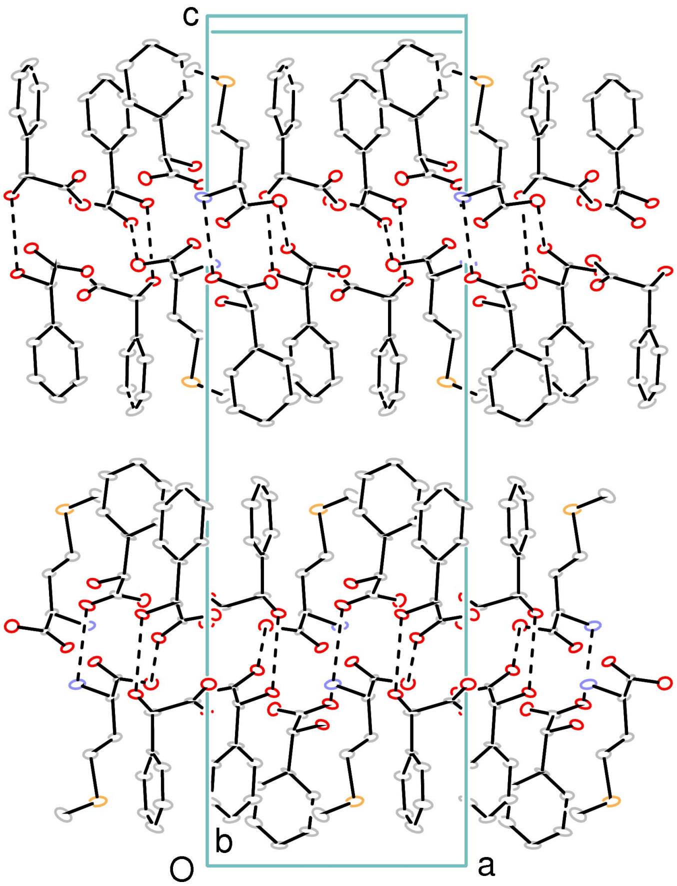


Figure 2

The packing of (I), viewed along the crystallographic *b* axis, showing the alternate hydrophilic and hydrophobic layers. Dashed lines represent hydrogen bonds. H atoms have been omitted for clarity.

[(*R*)-methionine]. Whereas racemic mixtures of mandelic acid are used in the preparation of (I), only one enantiomer (*R* configuration) occurs in the crystals of (I). The (*R*)-methioninium cation displays the most stable conformation, *i.e.* an *anti* conformation for all single bonds. Thus atoms C2–C5 and S are essentially coplanar, the maximum deviation being 0.043 (7) Å for atom C3.

The differences between C—O bond distances in each carboxy group are 0.140 (16) Å (C1 carboxy), 0.082 (17) Å (C11 carboxy) and 0.108 (16) Å (C21 carboxy), while the corresponding difference in the C31 carboxylate group is 0.068 (18) Å. All carboxy H atoms form O—H···O hydrogen bonds in the crystal structure of (I) (Table 2).

The molecular packing of (I) is presented in Fig. 2. The skeletons of all components display similar spatial orientations, and are oriented nearly parallel to each other. In the crystal structure of (I), the ions and molecules are arranged to form layers, with the hydrophilic groups on one side and the hydrophobic groups on the other side. The hydrophilic and hydrophobic layers alternate in the crystal structure along the crystallographic *c* axis. The components in the hydrophilic layers link to each other via N—H···O and O—H···O hydrogen bonds (Table 2), whereas in the hydrophobic layers they interact through van der Waals contacts.

Experimental

All reagents were commercially available and of analytical grade. (*R*)-Methionine (0.14g, 1mmol) and racemic mandelic acid (0.30g, 2mmol) were dissolved in a water/ethanol solution (20ml, 1:1). The solution was refluxed for 2 h, and then cooled to room temperature and filtered. Colorless single crystals of (I) were obtained from the filtrate after one week.

Crystal data

$C_5H_{12}NO_2S^+\cdot C_8H_7O_3^-\cdot C_8H_8O_3$
$M_r = 605.65$
Orthorhombic, $P2_12_12_1$
$a = 9.562$ (3) Å
$b = 9.830$ (3) Å
$c = 31.393$ (5) Å
$V = 2950.8$ (14) Å^3
$Z = 4$
$D_x = 1.363$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 5.6$–$14.6°$
$\mu = 0.17$ mm^{-1}
$T = 298$ (2) K
Prism, colorless
0.20 × 0.18 × 0.16 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3416 measured reflections
2974 independent reflections
1383 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$

$\theta_{max} = 25.0°$
$h = -5 \rightarrow 11$
$k = -5 \rightarrow 11$
$l = -19 \rightarrow 37$
3 standard reflections every 150 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.086$
$wR(F^2) = 0.250$
$S = 0.98$
2974 reflections
380 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.136P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

C1—O1	1.310 (12)	C21—O21	1.312 (11)
C1—O2	1.170 (11)	C21—O22	1.204 (11)
C11—O11	1.296 (12)	C31—O31	1.194 (12)
C11—O12	1.214 (12)	C31—O32	1.262 (13)
C4—S—C5	100.1 (6)	O21—C21—O22	127.0 (11)
O1—C1—O2	129.0 (11)	O31—C31—O32	126.4 (11)
O11—C11—O12	126.3 (12)		

Table 2

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O22^{i}	0.96	1.80	2.751 (10)	170
O11—H11···O32^{ii}	0.95	1.66	2.495 (10)	144
O13—H13···O23^{iii}	0.87	2.11	2.978 (8)	179
O21—H21···O12^{iv}	1.00	1.67	2.640 (10)	163
O23—H23···O32^{v}	0.87	2.02	2.679 (10)	131
O33—H33···O13	0.96	2.10	2.921 (11)	142
N—H1*A*···O31^{i}	0.89	2.10	2.973 (9)	168
N—H1*B*···O23	0.89	2.06	2.924 (11)	164
N—H1*C*···O33	0.89	1.96	2.833 (10)	166

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

H atoms on carboxy and hydroxy groups were located in a difference Fourier map and refined riding in their as-found positions, with fixed isotropic displacement parameters of 0.08 Å^2. Other H atoms were placed in calculated positions, with C—H = 0.93 (aromatic), 0.96 (methyl), 0.97 (methylene) or 0.98Å (methine) and N—H = 0.89Å, and were included in the final cycles of refinement as riding, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(N,C) (aminium and methyl) or 1.2$U_{\rm eq}$(C) (methylene, methine and aromatic). The absolute configuration of (I) could not be established in this analysis and was assigned on the basis of the known configuration of the starting reagent [(*R*)-methionine]. Friedel pairs were merged during the refinement.

Data collection: *MSC*/*AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC*/*AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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