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Bis(cinchonidinium) L-tartrate dihydrate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.130
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.

Bis-(3*R*,4*S*,8*S*,9*R*)-cinchonidinium (2*R*,3*R*)-tartrate dihydrate, $2C_{19}H_{23}N_2O_2^{+}\cdot C_4H_4O_6^{2-}\cdot 2H_2O$, is a hydrated salt of cinchonidine, in which the two protonated quinuclidinic nitrogen groups interact with the ionized carboxylate group of the tartrate; the latter has twofold symmetry. The water molecule interacts with the hydroxyl group of the cation and the O atoms of the carboxylate residues to afford a three-dimensional network structure.

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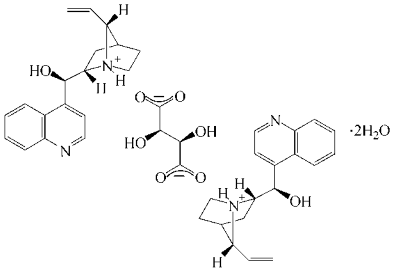
Comment

Cincona alkaloids are widely used for the resolution of racemic acids and tartaric acid is commonly employed for the separation of optically active bases (Eliel, 1996; Collet, 1999). Amongst these alkaloids, (3*R*,4*S*,8*R*,9*S*)-cinchonan-9-ol owes its physiological activity to the stereochemistry of the chiral atoms C8 and C9; also to the amino group (on the C8 atom) and the hydroxyl group (on the C9 atom) forming hydrogen bonds with receptors. This alkaloid, when treated with one molar equivalent of tartaric acid, affords cinchoninium–bitartrate tetrahydrate (Puliti *et al.*, 2001); the bitartrate anions are linked by a carboxyl–hydroxyl hydrogen bond into a chain running along the *b* axis of the monoclinic unit cell. When the stereochemistry of the alkaloid is altered to 8*S*,9*R*, as in (3*R*,4*S*,8*S*,9*R*)-cinchonan-9-ol, the synthesis furnishes the title diammonium tartrate, (I), as a dihydrate (see Scheme, Fig. 1 and Table 1). The asymmetric unit comprises the cinchonidinium cation, one water molecule and half the tartrate dianion; the latter lies on a twofold axis.



(I)

The carboxylic acid group of the tartrate anion shows almost equivalent bond lengths, consistent with deprotonation. The carboxyl atom O2 is strongly hydrogen bonded to the aliphatic ammonium group [N···O = 2.694 (3) Å] and the atom O4 is linked to the hydroxyl group within the same anion [O···O = 2.616 (3) Å]. The water molecule interacts with the hydroxyl group of the cation and two O atoms of carboxylate groups, derived from two different anions, to afford a three-dimensional network motif. Hydrogen-bonding contacts are summarized in Table 2. The crystal packing is somewhat less compact than that of cinchoninium–bitartrate tetrahydrate, as

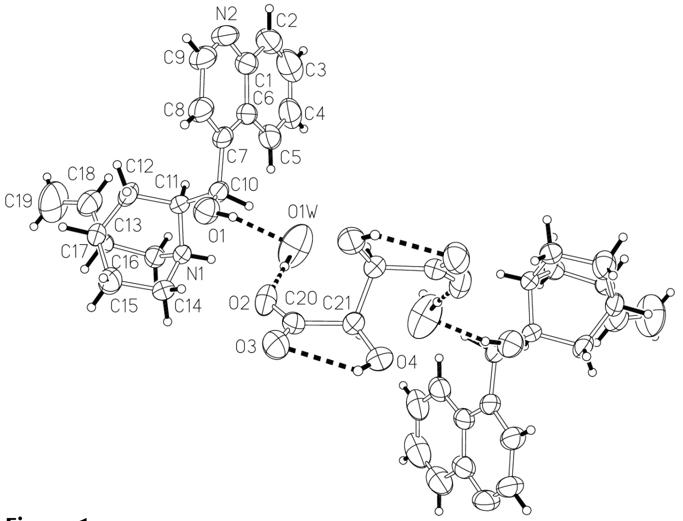


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with ellipsoids shown at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

noted from the densities of the two salts, which are 1.308 and 1.332 Mg m^{-3} for the di- and tetrahydrates, respectively (Puliti *et al.*, 2001).

Experimental

Cinchonidine (2.94 g, 10 mmol) and L-tartaric acid (0.75 g, 5 mmol) were dissolved in a small volume of 50:50 ethanol–water; the solution was kept at about 333 K for 10 h. The dihydrate separated from the solution in 80% yield. Found (calculated) for $C_{42}H_{54}N_4O_{10}$: C 64.8 (65.1), H 7.1 (7.0), N 7.0% (7.2%). IR (KBr pellet): CO_2 (asymmetric) 1593, 1509; CO_2 (symmetric) 1457, 1419, 1391 cm^{-1}.

Crystal data

$2C_{19}H_{23}N_2O^+ \cdot C_4H_4O_6^{2-} \cdot 2H_2O$
$M_r = 774.89$
Monoclinic, $C2$
$a = 19.960$ (3) Å
$b = 6.625$ (2) Å
$c = 15.530$ (2) Å
$\beta = 106.68$ (1)°
$V = 1967.2$ (7) Å^3
$Z = 2$
$D_x = 1.308$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15.1$–$19.2°$
$\mu = 0.09$ mm^{-1}
$T = 296$ (2) K
Block, colorless
0.38 × 0.30 × 0.22 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.498$, $T_{\max} = 0.876$
4178 measured reflections
2094 independent reflections
1703 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 26.0°$
$h = -24 \rightarrow 24$
$k = -8 \rightarrow 0$
$l = -19 \rightarrow 19$
2 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.130$
$S = 1.11$
2094 reflections
268 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 0.1359P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C10	1.413 (4)	C6—C7	1.423 (5)
O2—C20	1.267 (4)	C7—C8	1.369 (5)
O3—C20	1.236 (5)	C7—C10	1.519 (4)
O4—C21	1.407 (4)	C8—C9	1.414 (5)
N1—C14	1.497 (5)	C10—C11	1.528 (4)
N1—C11	1.505 (3)	C11—C12	1.539 (4)
N1—C16	1.505 (5)	C12—C13	1.518 (4)
N2—C9	1.298 (7)	C13—C17	1.527 (6)
N2—C1	1.363 (6)	C13—C15	1.539 (5)
C1—C2	1.409 (7)	C14—C15	1.525 (4)
C1—C6	1.429 (4)	C16—C17	1.548 (4)
C2—C3	1.366 (8)	C17—C18	1.497 (5)
C3—C4	1.399 (6)	C18—C19	1.284 (6)
C4—C5	1.366 (6)	C20—C21	1.530 (4)
C5—C6	1.410 (5)	C21—C21$^{\rm i}$	1.526 (5)
C14—N1—C11	113.7 (3)	C7—C10—C11	107.1 (2)
C14—N1—C16	109.6 (2)	N1—C11—C10	113.1 (2)
C11—N1—C16	107.8 (2)	N1—C11—C12	107.9 (2)
C9—N2—C1	117.6 (3)	C10—C11—C12	114.0 (3)
N2—C1—C2	118.8 (4)	C13—C12—C11	109.2 (2)
N2—C1—C6	122.7 (4)	C12—C13—C17	111.2 (3)
C2—C1—C6	118.5 (4)	C12—C13—C15	108.5 (3)
C3—C2—C1	121.6 (4)	C17—C13—C15	108.4 (3)
C2—C3—C4	120.1 (5)	N1—C14—C15	109.5 (3)
C5—C4—C3	119.8 (5)	C14—C15—C13	108.7 (3)
C4—C5—C6	121.9 (3)	N1—C16—C17	109.2 (3)
C5—C6—C7	124.7 (3)	C18—C17—C13	112.7 (3)
C5—C6—C1	118.0 (4)	C18—C17—C16	112.9 (3)
C7—C6—C1	117.2 (4)	C13—C17—C16	108.2 (3)
C8—C7—C6	118.7 (3)	C19—C18—C17	124.4 (4)
C8—C7—C10	119.9 (3)	O3—C20—O2	125.1 (3)
C6—C7—C10	121.3 (3)	O3—C20—C21	117.5 (3)
C7—C8—C9	119.0 (4)	O2—C20—C21	117.4 (3)
N2—C9—C8	124.7 (4)	O4—C21—C21$^{\rm i}$	110.5 (2)
O1—C10—C7	111.7 (3)	O4—C21—C20	110.4 (3)
O1—C10—C11	110.0 (2)	C21$^{\rm i}$—C21—C20	108.8 (3)

Symmetry code: (i) $2 - x, y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O1W	0.84 (1)	1.91 (2)	2.722 (4)	162 (4)
N1—H1N···O2$^{\rm i}$	0.87 (1)	1.83 (1)	2.694 (3)	177 (3)
O4—H4O···O3	0.85 (1)	2.12 (4)	2.616 (3)	117 (4)
O1W—H1W1···O2	0.87 (1)	1.86 (2)	2.712 (5)	167 (5)
O1W—H1W2···O3$^{\rm i}$	0.86 (1)	2.23 (2)	3.071 (5)	166 (5)

Symmetry code: (i) $x, y - 1, z$.

The H atoms bonded to the N and O atoms were located and refined, subject to N—H = O—H = 0.85±0.01 Å; for the water H atoms, the H···H distance was set to 1.39±0.01 Å. The C-bound H atoms were included in the riding-model approximation. The $U_{\rm iso}$ values of all H atoms were set at 1.2 times those of their parent atoms. The calculation of the Flack (1983) parameter was suppressed by the use of the MERG 4 instruction in *SHELXL*97. The absolute structure was determined on the basis of the known configuration of L-tartrate.

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *VAX/PC*; data reduction: *XCAD*4 (Harms, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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