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2,2′-Diamino-4,4′-bi-1,3-thiazolium (2*R*,3*R*)-tartrate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.076
Data-to-parameter ratio = 15.2

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

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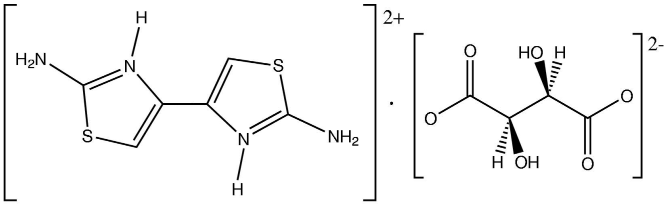
Crystals of the title chiral compound, $C_6H_8N_4S_2^{2+}\cdot C_4H_4O_6^{2-}$, were obtained from a solution containing diaminobithiazole (DABT) and racemic tartaric acid. The crystal structure consists of a protonated DABT dications (H_2DABT) and (2*R*,3*R*)-tartrate dianions linked *via* hydrogen bonding. An overlapped arrangement and a centroid-to-centroid separation of 3.4620 (11) Å between nearly parallel thiazole rings of adjacent H_2DABT cations indicate the existence of π–π stacking in the crystal structure.

Comment

Transition metal complexes with 2,2′-diamino-4,4′-bithiazole (DABT) or its derivatives have shown interesting properties and potential applications in many fields (Fisher *et al.*, 1985). During the preparation of a silver complex incorporating DABT, crystals of the title diaminobithiazolium salt, (I), were unexpectedly obtained.


(I)

The structure of (I) is shown in Fig. 1. The compound consists of protonated DABT dictations (H_2DABT) and (2*R*,3*R*)-tartrate dianions. The H_2DABT cation displays a nearly planar *trans* configuration and the dihedral angle between the two thiazole mean planes is 7.02 (4)°. The nearly identical N1—C1 [1.326 (3) Å] and N4—C4 [1.319 (3) Å] bonds suggest the existence of electron delocalization between the thiazole rings and the amino groups. The shorter S—C bond distances and smaller C—S—C bond angles (Table 1) may imply constraint within the thiazole rings.

The C7—C8—C9—C10 torsion angle of 174.1 (2)° shows that the tartrate anion has a nearly planar carbon skeleton. The carboxyl groups are tilted with respect to the carbon skeleton, with dihedral angles of 53.0 (2) and 63.9 (2)°. The tartrate anions link with H_2DABT cations *via* N—H···O hydrogen bonds (Fig. 2), while tartrate anions link to each other *via* O—H···O hydrogen bonds (Table 2).

An overlapped arrangement of adjacent H_2DABT cations, related by a twofold axis, is observed (Fig. 2). The centroid-to-centroid distance of 3.4620 (11) Å shows there is π–π stacking between the S1 thiazole ring and the S2^{v} thiazole ring [symmetry code: (v) y, x, $1 - z$].

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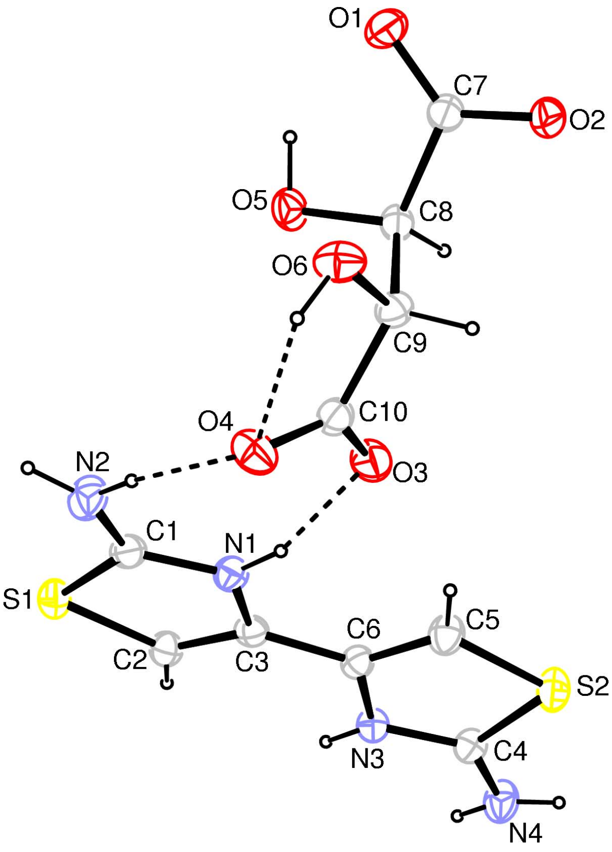

Figure 1

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the hydrogen bonding.

Experimental

Microcrystals of DABT were obtained using the method reported by Erlenmeyer (1948). An aqueous solution (20 ml) containing DABT (0.20 g, 1 mmol) and $AgNO_3$ (0.17 g, 1 mmol) was mixed with another aqueous solution (10 ml) containing racemic tartaric acid (0.15 g, 1 mmol) and NaOH (0.08 g, 2 mmol). The mixture was refluxed for 1 h and filtered. Yellow single crystals of (I) were obtained from the filtrate after 2 d.

Crystal data

$C_6H_8N_4S_2^{2+}\cdot C_4H_4O_6^{2-}$
$M_r = 348.36$
Hexagonal, $P3_221$
$a = 11.0122$ (7) Å
$c = 18.8285$ (14) Å
$V = 1977.4$ (2) Å^3
$Z = 6$
$D_x = 1.755$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3278 reflections
$\theta = 2.5$–$26.0°$
$\mu = 0.44$ mm^{-1}
$T = 295$ (2) K
Prism, yellow
0.40 × 0.33 × 0.31 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.835$, $T_{max} = 0.878$
18 080 measured reflections

3030 independent reflections
2895 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -24 \rightarrow 23$

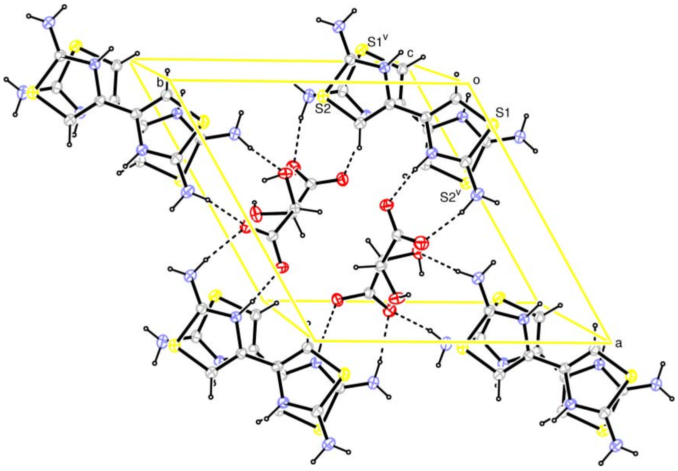

Figure 2

A packing diagram for (I), showing the π–π stacking between the thiazole rings and the hydrogen bonding between cations and anions (dashed lines) [symmetry code: (v) $y, x, 1 - z$].

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.076$
$S = 1.06$
3030 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.5513P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 1280 Friedel pairs
Flack parameter: −0.03 (6)

Table 1

Selected geometric parameters (Å, °).

S1—C1	1.731 (2)	S2—C4	1.745 (2)
S1—C2	1.730 (2)	S2—C5	1.735 (2)
C1—S1—C2	90.0 (1)	C4—S2—C5	89.7 (1)

Table 2

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3	0.89	1.79	2.647 (2)	161
N2—H2*A*···O1^{i}	0.82	2.04	2.819 (3)	158
N2—H2*B*···O4	0.91	1.97	2.867 (3)	169
N3—H3···O2^{ii}	0.87	1.77	2.622 (2)	169
N4—H4*A*···O1^{ii}	0.85	2.05	2.864 (2)	160
N4—H4*B*···O5^{iii}	0.84	2.09	2.889 (3)	157
O5—H5*A*···O4^{iv}	0.98	2.06	2.975 (2)	154
O6—H6*A*···O4	0.89	2.08	2.612 (2)	118
C2—H2···O2^{ii}	0.93	2.36	3.216 (3)	153
C5—H5···O3	0.93	2.43	3.280 (3)	152
C8—H8···O3^{v}	0.98	2.59	3.552 (3)	165

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

H atoms bound to C atoms were placed in calculated positions, with C—H = 0.93 Å (aromatic) or 0.98 Å (methine), and included in the final cycles of refinement in a riding model, with $U_{iso}(H) = 1.2U_{eq}$

of the carrier atoms. All other H atoms were located in a difference Fourier map and refined as riding in their as-found positions relative to their corresponding O or N atoms, with a fixed $U_{iso}(H)$ of 0.05 Å^2.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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