organic papers

2,2′-Diamino-4,4′-bi-1,3-thiazolium fumarate

Jia-Geng Liu,ᵃ Duan-Jun Xuᵃ* and Wei-Lin Sunᵇ

ᵃDepartment of Chemistry, Zhejiang University, Hangzhou, People's Republic of China, and ᵇDepartment of Polymer Science, Zhejiang University, Hangzhou, People's Republic of China

Correspondence e-mail: xudj@mail.hz.zj.cn

The title compound, $C_6H_8N_4S_2^{2+} \cdot C_4H_2O_4^{2-}$, consists of a diaminobithiazole (DABT) cation and a fumarate anion. The cation and anion are both located on inversion centers. Both ions display a planar configuration and link to each other through hydrogen bonding between carboxyl and amino groups, as well as through weak C—H···O hydrogen bonding between thiazole and carboxyl groups. The C—N(amino) bond distance of 1.323 (4) Å suggests the existence of electron delocalization between the thiazole ring and the amino group.

Comment

Transition metal complexes with 2,2′-diamine-4,4′-bithiazole (DABT) or its derivatives have shown interesting properties and potential application in many fields (Waring, 1981; Fisher *et al.*, 1985). A series of metal complexes with DABT has been prepared in our laboratory (Liu *et al.*, 2001). As a part of this investigation, the X-ray structure of the title DABT fumarate, (I), is presented here.


(I)
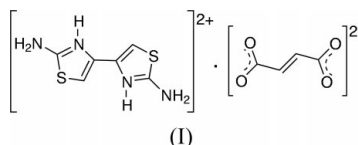
The structure of (I) is shown in Fig. 1 and consists of a protonated DABT cation and a fumarate anion, both being located on crystallographic inversion centers. The DABT cation displays a planar *trans* configuration, which agrees with that found in 2,2′-diamino-4,4′-1,3-thiazolium dichloride (Liu *et al.*, 2002), but differs from the *cis* configuration found in DABT–metal complexes (Tian *et al.*, 1996; Liu *et al.*, 2001). The N3—C2 distance of 1.333 (4) Å within the DABT cation is essentially identical to the values of 1.335 (6) and 1.322 (3) Å found in the dichloride (Liu *et al.*, 2002) and the Cuᴵᴵ complex (Liu *et al.*, 2001), respectively, but significantly longer than the distance of 1.309 (2) Å in the neutral DABT molecule (Liu *et al.*, 2003). The N2—C2 bond distance of 1.323 (4) Å suggests the existence of electron delocalization between the thiazole ring and the amino group.

The carboxyl groups of the fumarate anion are coplanar with the carbon skeleton, the maximum atomic deviation from the mean plane defined by all atoms of the fumarate being 0.0806 (14) Å (O1). The fumarate anions link with DABT cations through classic hydrogen bonding between the carboxyl and amino groups and weak C—H···O hydrogen bonding between the carboxyl and thiazole ring, forming a three-dimensional supramolecular structure, as shown in Fig. 2.
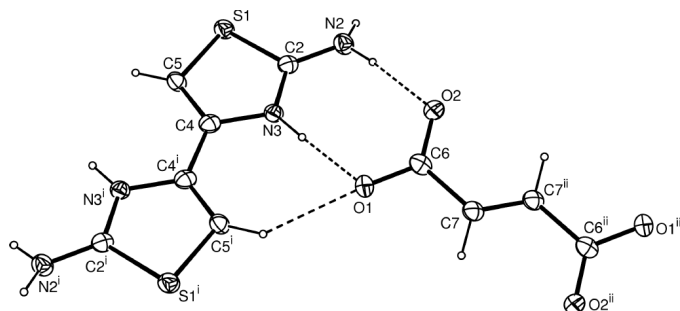
Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Dashed lines indicate hydrogen-bonding interactions. [Symmetry codes: (i) $2 - x, -y, -z$; (ii) $-x, 1 - y, -z$.]
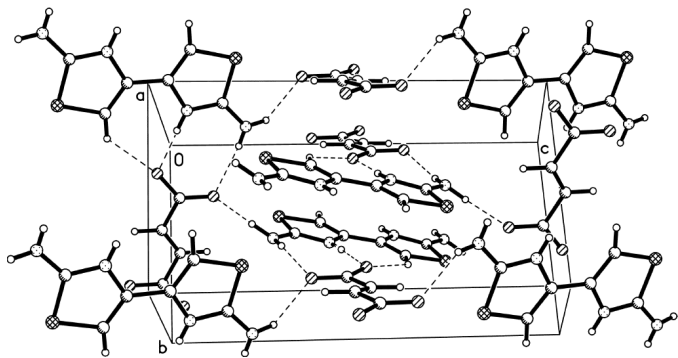
Figure 2
A view of the molecular packing of (I), with dashed lines indicating hydrogen-bonding interactions.

Experimental

Fine crystals of DABT were obtained in the manner reported by Erlenmeyer (1948). Single crystals of (I) were obtained from an aqueous solution, as a by-product, during the preparation of a BADT complex of Mn^{II} bridged by fumarate.

Crystal data

$C_6H_8N_4S_2{}^{2+} \cdot C_4H_2O_4{}^{2-}$	$D_x = 1.750$ Mg m^{-3}
$M_r = 314.34$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3028
$a = 5.2834 (17)$ Å	reflections
$b = 7.936 (3)$ Å	$\theta = 3.2$–$26.5°$
$c = 14.370 (5)$ Å	$\mu = 0.47$ mm^{-1}
$\beta = 98.164 (6)°$	$T = 298 (2)$ K
$V = 596.4 (4)$ Å^3	Prism, colorless
$Z = 2$	$0.32 \times 0.28 \times 0.20$ mm

Data collection

Rigaku R-AXIS-RAPID diffractometer	1359 independent reflections
	874 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.095$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$\theta_{max} = 27.5°$
$T_{min} = 0.86$, $T_{max} = 0.91$	$h = -5 \rightarrow 6$
3650 measured reflections	$k = -10 \rightarrow 9$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.062P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.050$	$+ 0.0525P]$
$wR(F^2) = 0.137$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
1359 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
91 parameters	$\Delta\rho_{min} = -0.68$ e Å^{-3}
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H21···O2	0.83	2.02	2.831 (3)	164
N2—H22···O2^{iii}	0.86	2.09	2.832 (3)	145
N3—H3···O1	0.86	1.80	2.658 (3)	172
C5—H5···O1^i	0.93	2.31	3.181 (4)	155

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

Amine H atoms were located in a difference Fourier map and were included in the final cycles of refinement, with fixed positional parameters and U_{iso} of values of 0.04 Å^2. Other H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and included in the final cycles of refinement as riding, with U_{iso}(H) = $1.2U_{eq}$ of the carrier atoms.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC and Rigaku, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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