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2,2′-Diamino-4,4′-bi-1,3-thiazol-3,3′-diium bis(2,2′-diamino-4,4′-bi-1,3-thiazol-3-ium) tetrakis(2-nitrobenzoate)

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Key indicators

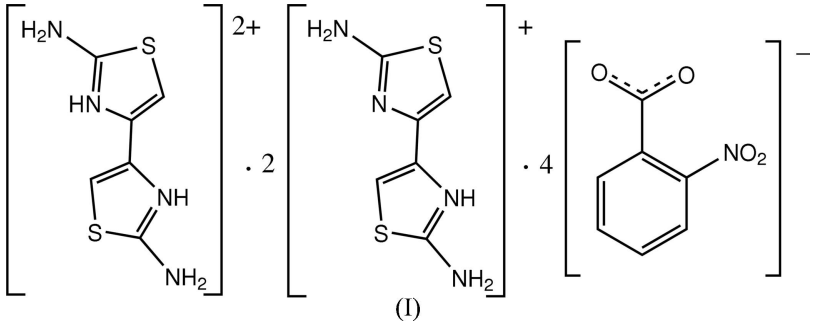
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.108
Data-to-parameter ratio = 16.0

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

The crystal structure of the title compound, $C_6H_8N_4S_2^{2+}\cdot 2C_6H_7N_4S_2^{+}\cdot 4C_7H_4NO_4^{-}$, comprises diprotonated diaminobithiazole (DABT) dications located on inversion centers, monoprotonated DABT cations and nitrobenzoate anions. The relatively short C—N(amino) bond distances, ranging from 1.310 (2) to 1.350 (2) Å, indicate electron delocalization between the amino groups and thiazole rings. Intermolecular N—H···O and N—H···N hydrogen bonds stabilize the crystal packing.

Comment

Transition metal complexes containing the diaminobithiazole (DABT) ligand or its derivatives have attracted our attention because of their interesting magnetic (Sun *et al.*, 1997) and biological activities: they can serve as effective inhibitors of the DNA synthesis of tumor cells (Waring, 1981; Fisher *et al.*, 1985). During the preparation of an Ag^{I} complex of DABT, the title DABT salt, (I), was unexpectedly obtained.



(I)

The structure of (I) is shown in Fig. 1. The triclinic unit cell contains one diprotonated dication, H_2DABT^{2+}, located on an inversion center, two protonated cations, $HDABT^{+}$, and four nitrobenzoate anions. Both H_2DABT^{2+} and $HDABT^{+}$ display a *trans* planar configuration, which agrees with that found for neutral, uncoordinated DABT (Liu & Xu, 2003). The C—N(amino) bond distances (Table 1) are much shorter than the normal single C—N bond, indicating electron delocalization between the amino and thiazole groups. It is notable that the C—N(amino) bonds in the protonated thiazole rings, *i.e.* N2—C3 and N6—C9, are significantly shorter than the N4—C5 bond in the neutral thiazole ring (Table 1). This is consistent with the DABT salts reported previously (Liu & Xu, 2005; Liu *et al.*, 2002; Liu, Xu & Sun, 2003).

Two carboxylate groups, C17/O11/O12 and C27/O21/O22, make different dihedral angles with the attached benzene rings [39.41 (9) and 13.1 (2)°, respectively], leading to the formation of N—H···O hydrogen bonds (Table 2) between

the anions and neighboring protonated DABT cations (Fig. 1). An extensive network of intermolecular N—H···O and N—H···N hydrogen bonds (Table 2) stabilizes the crystal packing.

Experimental

An aqueous solution (20 ml) of DABT (0.20 g, 1 mmol) and $AgNO_3$ (0.17 g, 1 mmol) was mixed with another aqueous solution (10 ml) of 2-nitrobenzoic acid (0.33 g, 2 mmol) and NaOH (0.08 g, 2 mmol). The mixture was refluxed for 6 h. After cooling to room temperature, the solution was filtered. Yellow single crystals of (I) were obtained from the filtrate after 20 d.

Crystal data

$C_6H_8N_4S_2^{2+}\cdot 2C_6H_7N_4S_2^{+}\cdot 4C_7H_4NO_4^{-}$
$M_r = 1263.34$
Triclinic, $P\overline{1}$
$a = 7.6594\ (11)$ Å
$b = 13.3257\ (12)$ Å
$c = 14.1456\ (12)$ Å
$\alpha = 72.716\ (6)^\circ$
$\beta = 85.868\ (6)^\circ$
$\gamma = 74.749\ (6)^\circ$
$V = 1330.0\ (3)$ Å^3
$Z = 1$
$D_x = 1.577$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4530 reflections
$\theta = 2.8$–25.0°
$\mu = 0.34$ mm^{-1}
$T = 295\ (2)$ K
Prism, yellow
0.30 × 0.25 × 0.14 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.882$, $T_{max} = 0.950$
12059 measured reflections
6065 independent reflections
4714 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 27.5^\circ$
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.108$
$S = 1.02$
6065 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.2823P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected bond lengths (Å).

N1—C1	1.3955 (19)	N4—C5	1.350 (2)
N1—C3	1.3351 (19)	N5—C7	1.3928 (19)
N2—C3	1.311 (2)	N5—C9	1.3359 (19)
N3—C4	1.3948 (19)	N6—C9	1.310 (2)
N3—C5	1.313 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O11	0.92	1.75	2.6597 (19)	171
N2—H2*A*···O12	0.86	1.97	2.819 (2)	168
N2—H2*B*···O21^{i}	0.86	1.98	2.788 (2)	157
N4—H4*A*···N3^{ii}	0.86	2.22	3.066 (2)	167
N5—H5···O22	0.97	1.67	2.6384 (19)	174
N6—H6*A*···O21	0.86	1.93	2.773 (2)	166
N6—H6*B*···O12^{i}	0.86	1.99	2.788 (2)	154

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+2, -y+1, -z+1$.

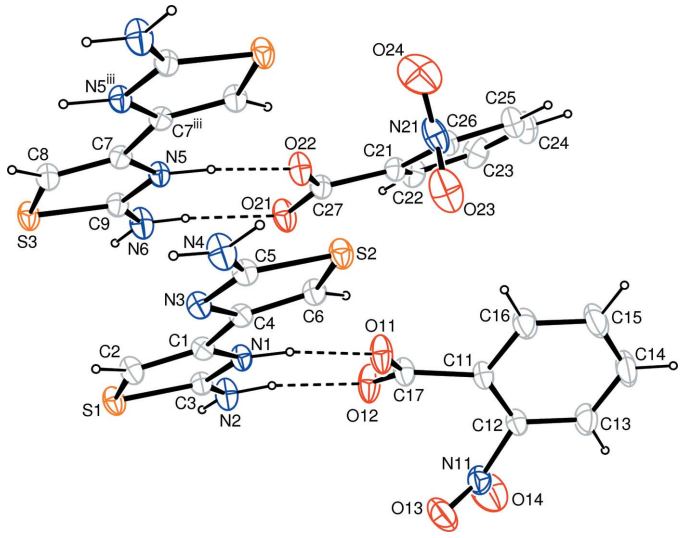


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate the hydrogen bonds [symmetry code: (iii) $1-x, 1-y, 1-z$].

Atoms H1 and H5, attached to N1 and N5, respectively, were located in a difference Fourier map and refined as riding, with $U_{iso}(H) = 1.5U_{eq}(N)$. The remaining H atoms were placed in calculated positions and refined as riding, with C—H = 0.93 Å, N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}$ of the parent atom.

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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