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4,4′-Bipyridine-1,1′-diium bis(1,3-benzothiazole-2-thiolate)

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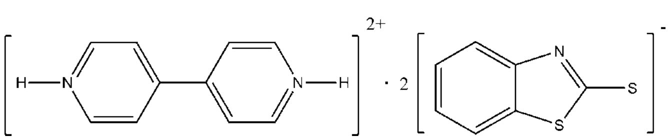
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.008 Å; R factor = 0.060; wR factor = 0.203; data-to-parameter ratio = 14.6.

In the title salt, $C_{10}H_{10}N_2^{2+}\cdot 2C_7H_4NS_2^-$, the complete 4,4′-bipyridine-1,1′-diium dication is generated by a center of symmetry. In the crystal, N—H⋯N hydrogen bonds are observed between the cations and anions.

Related literature

For ligands based on 2-mercaptobenzothiazole in coordination chemistry, see: Chen *et al.* (2010) and for ligands based on 4,4′-bipyridine, see: Biradha *et al.* (1999); Ren *et al.* (2004); Tao *et al.* (2000); Tong *et al.* (2000); Xu *et al.* (2012). For a related structure, see: Deng *et al.* (2005).



Experimental

Crystal data

$C_{10}H_{10}N_2^{2+}\cdot 2C_7H_4NS_2^-$
M_r = 490.66
Monoclinic, $P2_1/c$
a = 14.3909 (13) Å
b = 5.6670 (4) Å
c = 15.5471 (14) Å
β = 109.023 (2)°
V = 1198.67 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.42 mm^{-1}
T = 298 K
0.32 × 0.30 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.878, T_{max} = 0.900
5663 measured reflections
2116 independent reflections
990 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.203
S = 1.04
2116 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2⋯N1^{i}	0.86	1.93	2.790 (6)	178

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JJ2151).

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Acta Cryst. (2012). E**68**, o3450 [doi:10.1107/S1600536812047058]

4,4′-Bipyridine-1,1′-diium bis(1,3-benzothiazole-2-thiolate)

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S1. Comment

The 4,4′-bipyridine lignad is ideal for forming supramolecular structures. Many examples in coordination with multifarious metals are observed (Biradha *et al.*, 1999; Tong *et al.*, 2000; Tao *et al.*, 2000; Ren *et al.*, 2004; Xu *et al.*, 2012). However, to our best knowledge, only a few Ag(I)-Hmbt (Hmbt = 2-mercaptobenzothiazole) framework structures have been reported (Chen *et al.*, 2010). In our work synthesizing an Ag(I)-Hmbt complex containing the 4,4′-bipyridine, the title compound, (I), $(C_{10}H_{10}N_2).(C_7H_4NS_2)_2$ was unexpectedly obtained.

The crystal structure of the title compound, (I), consists of one mbt (mercaptobenzothiazole) anion and one 4-pyridyl unit containg a center of symmetry which upon expansion produces a 4,4′-bipyridine-1,1′-diium cation and two mbt cations in the asymmetric unit (Fig. 1). Crystal packing reveals that N—H···N intermolecular hydrogen bonds are observed between the centrosymmetric 4,4′-bipyridine-1,1′-diium cation and two mbt anions (Fig. 2; Table 1). These observed hydrogen bonds are similar to those reported in a similar and related compound, $(C_{10}H_8N_2)(C_2H_3N_3S_2)_2$, (Deng *et al.*, 2005).

S2. Experimental

A mixture of AgBr (0.2 mmol) and 2-mercaptobenzothiazole (0.2 mmol) in MeOH and CH_2Cl_2 (10 mL, *v*/*v* = 1:1) was stirred for 2 h and triphenylphosphine (PPh_3)(0.2 mmol) was added to the mixture which was stirred for another 5 h. The insoluble residues were removed by filtration. The filtrate was then evaporated slowly at room temperature for a week to yield colorless crystalline products. Anal. Calc. for $C_{24}H_{18}N_4S_4$: C, 58.70; H, 3.67; N, 11.41. Found: C, 58.49; H, 3.79; N, 11.22%. Melting point: 427–431°K.

S3. Refinement

All H atoms were located in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded (U_{iso}(H) = 1.2Ueq). C—H hydrogen atoms (aromatic) were included with distance set to 0.93 Å and amide N—H hydrogen atoms were included with distance set to 0.86 Å.

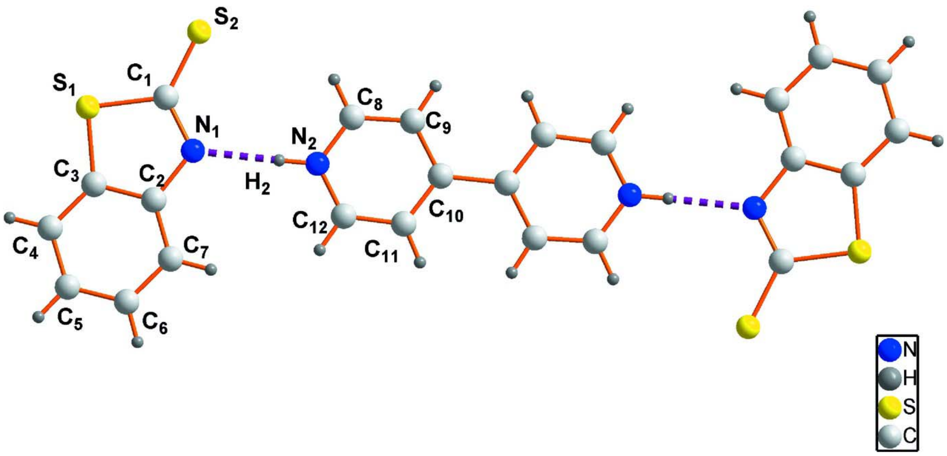

Figure 1

The molecular entities of the title compound, showing the atom-numbering scheme of the 4-pyridyl and mercaptobenzothiazole units and the symmetry expanded 4,4′-bipyridine-1,1′-diium cation and two mbt cation units with displacement ellipsoids drawn at the 50% probability level.

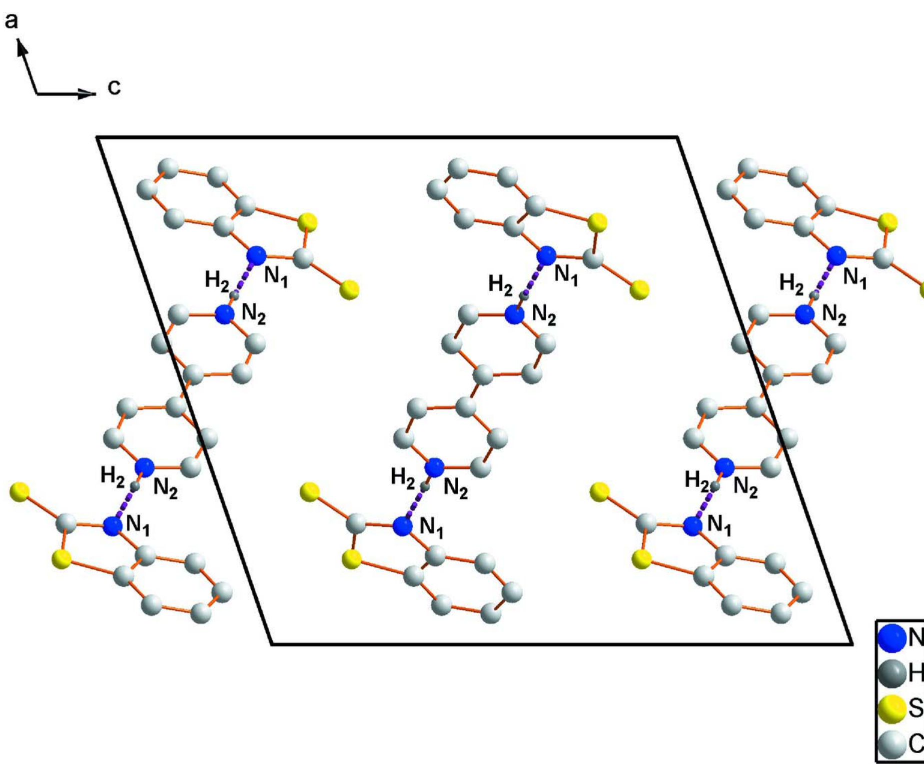

Figure 2

A view of the packing in (I) along the *b* axis. Dashed lines indicate N—H···N hydrogen bonds. H atoms not involved in hydrogen bonding have been removed for clarity.

4,4′-Bipyridine-1,1′-diium; bis(1,3-benzothiazole-2-thiolate)

Crystal data

$C_{10}H_{10}N_2^{2+}\cdot 2C_7H_4NS_2^-$
M_r = 490.66
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 14.3909 (13) Å
b = 5.6670 (4) Å
c = 15.5471 (14) Å
β = 109.023 (2)°
V = 1198.67 (17) Å^3
Z = 2
$F(000)$ = 508
D_x = 1.359 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1198 reflections
θ = 2.7–20.7°
μ = 0.42 mm^{-1}
T = 298 K
Block, colorless
0.32 × 0.30 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.878, T_{max} = 0.900
5663 measured reflections
2116 independent reflections
990 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 25.0°, θ_{min} = 2.7°
h = −17→11
k = −6→6
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.203
S = 1.04
2116 reflections
145 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 0.6601P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.2335 (3)	0.3414 (7)	0.7956 (2)	0.0629 (11)
N2	0.6509 (3)	0.4638 (7)	0.6145 (3)	0.0700 (11)
H2	0.6875	0.5792	0.6419	0.084*
S1	0.16856 (12)	0.6851 (3)	0.68804 (10)	0.1018 (7)

S2	0.30080 (16)	0.3128 (4)	0.65559 (11)	0.1352 (9)
C1	0.2387 (4)	0.4264 (10)	0.7171 (3)	0.0812 (16)
C2	0.1755 (3)	0.4737 (9)	0.8346 (3)	0.0586 (12)
C3	0.1353 (4)	0.6727 (10)	0.7852 (3)	0.0720 (14)
C4	0.0782 (4)	0.8244 (11)	0.8160 (5)	0.102 (2)
H4	0.0515	0.9598	0.7835	0.122*
C5	0.0617 (5)	0.7703 (13)	0.8960 (6)	0.112 (2)
H5	0.0217	0.8680	0.9170	0.135*
C6	0.1030 (5)	0.5758 (13)	0.9448 (4)	0.0991 (19)
H6	0.0921	0.5448	0.9995	0.119*
C7	0.1601 (3)	0.4255 (9)	0.9152 (3)	0.0700 (14)
H7	0.1879	0.2929	0.9491	0.084*
C8	0.5934 (4)	0.3548 (11)	0.6502 (4)	0.0888 (18)
H8	0.5926	0.4038	0.7070	0.107*
C9	0.5343 (4)	0.1726 (11)	0.6091 (4)	0.0888 (17)
H9	0.4955	0.0979	0.6385	0.107*
C10	0.5317 (3)	0.0987 (8)	0.5244 (3)	0.0549 (12)
C11	0.5936 (4)	0.2124 (10)	0.4888 (3)	0.0843 (17)
H11	0.5967	0.1676	0.4322	0.101*
C12	0.6507 (4)	0.3907 (11)	0.5350 (4)	0.0914 (19)
H12	0.6923	0.4653	0.5086	0.110*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.068 (2)	0.077 (3)	0.046 (2)	−0.008 (2)	0.0210 (19)	0.002 (2)
N2	0.060 (2)	0.070 (3)	0.072 (3)	−0.015 (2)	0.010 (2)	−0.002 (2)
S1	0.1082 (12)	0.1031 (13)	0.0740 (9)	−0.0164 (10)	0.0019 (8)	0.0351 (9)
S2	0.1740 (19)	0.177 (2)	0.0824 (11)	−0.0039 (16)	0.0806 (12)	0.0087 (12)
C1	0.086 (4)	0.105 (5)	0.051 (3)	−0.020 (3)	0.020 (3)	0.013 (3)
C2	0.057 (3)	0.059 (3)	0.054 (3)	−0.004 (2)	0.010 (2)	0.001 (2)
C3	0.063 (3)	0.058 (3)	0.077 (3)	−0.009 (3)	−0.002 (3)	0.005 (3)
C4	0.074 (4)	0.061 (4)	0.141 (6)	0.008 (3)	−0.004 (4)	0.000 (4)
C5	0.091 (5)	0.094 (6)	0.146 (7)	0.011 (4)	0.031 (5)	−0.035 (5)
C6	0.103 (5)	0.105 (5)	0.095 (4)	0.012 (4)	0.040 (4)	−0.018 (4)
C7	0.076 (3)	0.069 (3)	0.068 (3)	0.005 (3)	0.027 (3)	−0.004 (3)
C8	0.089 (4)	0.108 (5)	0.077 (4)	−0.031 (4)	0.038 (3)	−0.019 (3)
C9	0.085 (4)	0.116 (5)	0.081 (4)	−0.027 (4)	0.049 (3)	−0.015 (4)
C10	0.044 (3)	0.061 (3)	0.057 (3)	0.004 (2)	0.013 (2)	0.011 (2)
C11	0.099 (4)	0.103 (4)	0.054 (3)	−0.035 (4)	0.029 (3)	−0.007 (3)
C12	0.109 (4)	0.112 (5)	0.058 (3)	−0.040 (4)	0.033 (3)	0.001 (3)

Geometric parameters (Å, º)

N1—C1	1.337 (5)	C5—H5	0.9300
N1—C2	1.399 (5)	C6—C7	1.363 (7)
N2—C8	1.294 (6)	C6—H6	0.9300
N2—C12	1.303 (6)	C7—H7	0.9300

N2—H2	0.8600	C8—C9	1.358 (7)
S1—C3	1.728 (6)	C8—H8	0.9300
S1—C1	1.754 (6)	C9—C10	1.371 (6)
S2—C1	1.638 (6)	C9—H9	0.9300
C2—C7	1.370 (6)	C10—C11	1.355 (6)
C2—C3	1.381 (6)	C10—C10^{i}	1.487 (8)
C3—C4	1.378 (8)	C11—C12	1.352 (7)
C4—C5	1.375 (9)	C11—H11	0.9300
C4—H4	0.9300	C12—H12	0.9300
C5—C6	1.361 (9)		

C1—N1—C2	115.0 (4)	C5—C6—H6	119.3
C8—N2—C12	116.8 (5)	C7—C6—H6	119.3
C8—N2—H2	121.6	C6—C7—C2	118.6 (5)
C12—N2—H2	121.6	C6—C7—H7	120.7
C3—S1—C1	92.4 (3)	C2—C7—H7	120.7
N1—C1—S2	126.5 (5)	N2—C8—C9	123.5 (5)
N1—C1—S1	109.7 (4)	N2—C8—H8	118.3
S2—C1—S1	123.8 (3)	C9—C8—H8	118.3
C7—C2—C3	120.6 (5)	C8—C9—C10	120.1 (5)
C7—C2—N1	126.0 (4)	C8—C9—H9	120.0
C3—C2—N1	113.4 (4)	C10—C9—H9	120.0
C4—C3—C2	120.3 (5)	C11—C10—C9	115.6 (4)
C4—C3—S1	130.1 (5)	C11—C10—C10^{i}	121.7 (5)
C2—C3—S1	109.6 (4)	C9—C10—C10^{i}	122.7 (5)
C5—C4—C3	118.3 (6)	C12—C11—C10	120.3 (5)
C5—C4—H4	120.9	C12—C11—H11	119.8
C3—C4—H4	120.9	C10—C11—H11	119.8
C6—C5—C4	120.8 (6)	N2—C12—C11	123.7 (5)
C6—C5—H5	119.6	N2—C12—H12	118.1
C4—C5—H5	119.6	C11—C12—H12	118.1
C5—C6—C7	121.3 (6)		

C2—N1—C1—S2	179.6 (4)	C3—C4—C5—C6	1.9 (10)
C2—N1—C1—S1	0.0 (5)	C4—C5—C6—C7	−1.6 (10)
C3—S1—C1—N1	0.9 (4)	C5—C6—C7—C2	0.1 (8)
C3—S1—C1—S2	−178.8 (4)	C3—C2—C7—C6	1.0 (7)
C1—N1—C2—C7	−178.8 (4)	N1—C2—C7—C6	178.6 (5)
C1—N1—C2—C3	−1.1 (6)	C12—N2—C8—C9	−0.2 (8)
C7—C2—C3—C4	−0.6 (7)	N2—C8—C9—C10	−1.5 (9)
N1—C2—C3—C4	−178.5 (4)	C8—C9—C10—C11	2.4 (8)
C7—C2—C3—S1	179.5 (4)	C8—C9—C10—C10^{i}	−179.7 (5)
N1—C2—C3—S1	1.7 (5)	C9—C10—C11—C12	−1.8 (8)
C1—S1—C3—C4	178.7 (5)	C10^{i}—C10—C11—C12	−179.7 (5)
C1—S1—C3—C2	−1.5 (4)	C8—N2—C12—C11	0.9 (8)

C2—C3—C4—C5	−0.8 (8)	C10—C11—C12—N2	0.1 (9)
S1—C3—C4—C5	179.0 (5)		

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N1^{ii}	0.86	1.93	2.790 (6)	178

Symmetry code: (ii) −*x*+1, *y*+1/2, −*z*+3/2.