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## Structure Reports

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## 4,4'-Bipyridine-1,1'-dium bis(1,3-benzothiazole-2-thiolate)

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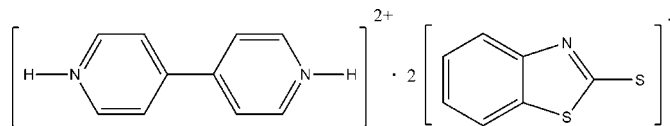
Received 2 September 2012; accepted 15 November 2012

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.008$  Å;  $R$  factor = 0.060;  $wR$  factor = 0.203; data-to-parameter ratio = 14.6.

In the title salt,  $\text{C}_{10}\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_4\text{NS}_2^-$ , the complete 4,4'-bipyridine-1,1'-dium dication is generated by a center of symmetry. In the crystal,  $\text{N}-\text{H} \cdots \text{N}$  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

 $\text{C}_{10}\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_4\text{NS}_2^-$  $M_r = 490.66$ Monoclinic,  $P2_1/c$  $a = 14.3909$  (13) Å $b = 5.6670$  (4) Å $c = 15.5471$  (14) Å $\beta = 109.023$  (2)° $V = 1198.67$  (17) Å<sup>3</sup> $Z = 2$ Mo  $K\alpha$  radiation $\mu = 0.42$  mm<sup>-1</sup> $T = 298$  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  $I > 2\sigma(I)$  $R_{\text{int}} = 0.055$ 

## 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

 $\Delta\rho_{\text{max}} = 0.29$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.26$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N2}-\text{H2} \cdots \text{N1}^i$	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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## supplementary materials

*Acta Cryst.* (2012). E68, o3450 [doi:10.1107/S1600536812047058]

**4,4'-Bipyridine-1,1'-dium bis(1,3-benzothiazole-2-thiolate)**

**Yu-Han Jiang, Qi-Ming Qiu, Min Liu, Qiong-Hua Jin and Cun-Lin Zhang**

**Comment**

The 4,4'-bipyridine ligand 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<sub>10</sub>H<sub>10</sub>N<sub>2</sub>).(C<sub>7</sub>H<sub>4</sub>NS<sub>2</sub>)<sub>2</sub> was unexpectedly obtained.

The crystal structure of the title compound, (I), consists of one mbt (mercaptobenzothiazole) anion and one 4-pyridyl unit containing a center of symmetry which upon expansion produces a 4,4'-bipyridine-1,1'-dium cation and two mbt anions 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'-dium 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<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>S<sub>2</sub>)<sub>2</sub>, (Deng *et al.*, 2005).

**Experimental**

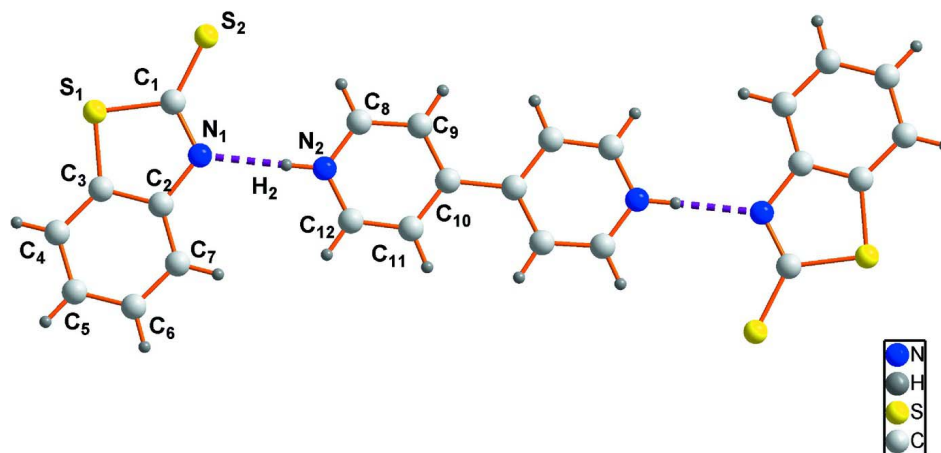
A mixture of AgBr (0.2 mmol) and 2-mercaptobenzothiazole (0.2 mmol) in MeOH and CH<sub>2</sub>Cl<sub>2</sub> (10 mL, *v/v* = 1:1) was stirred for 2 h and triphenylphosphine (PPh<sub>3</sub>) (0.2 mmol) was added to the mixture which was stirred for another 5 h. The insoluble residues were removed by filtration. The filtrate was then evaporated slowly at room temperature for a week to yield colorless crystalline products. Anal. Calc. for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>S<sub>4</sub>: C, 58.70; H, 3.67; N, 11.41. Found: C, 58.49; H, 3.79; N, 11.22%. Melting point: 427–431°K.

**Refinement**

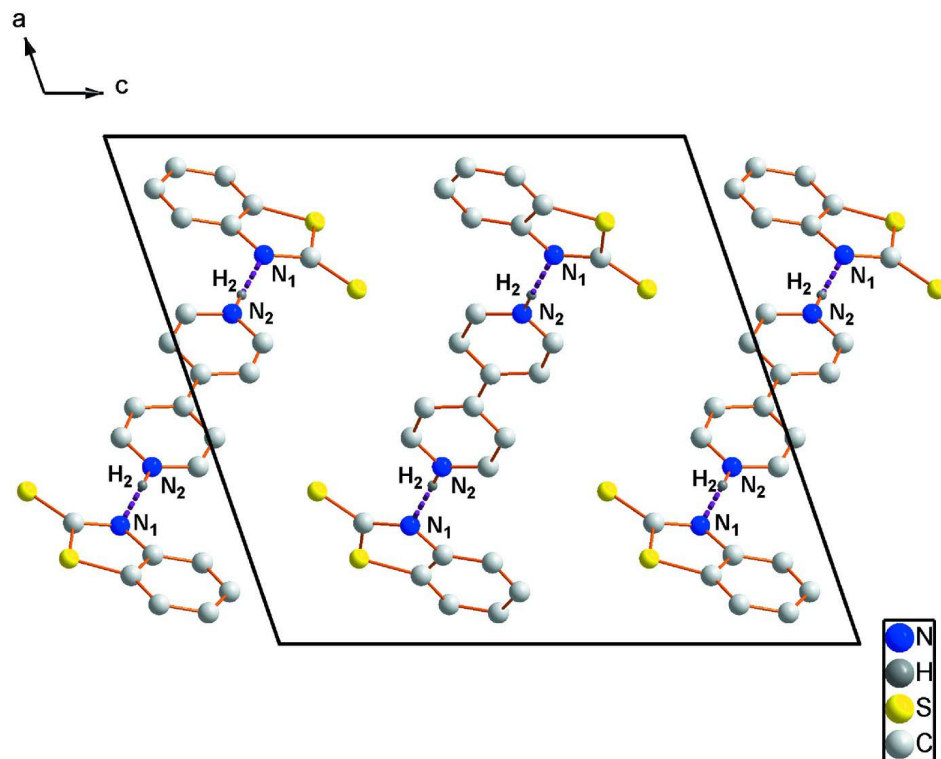
All H atoms were located in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded ( $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ ). C—H hydrogen atoms (aromatic) were included with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

**Computing details**

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINTE-Plus* (Bruker, 2007); data reduction: *SAINTE-Plus* (Bruker, 2007); 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* (Sheldrick, 2008).

**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'-dium 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  
 $\beta = 109.023$  (2)°  
 $V = 1198.67$  (17) Å<sup>3</sup>  
 $Z = 2$

$F(000) = 508$   
 $D_x = 1.359$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 1198 reflections  
 $\theta = 2.7$ – $20.7$ °  
 $\mu = 0.42$  mm<sup>-1</sup>  
 $T = 298$  K  
 Block, colorless  
 $0.32 \times 0.30 \times 0.26$  mm

*Data collection*

Bruker SMART CCD area-detector  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 phi and  $\omega$  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  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.055$   
 $\theta_{\max} = 25.0$ °,  $\theta_{\min} = 2.7$ °  
 $h = -17 \rightarrow 11$   
 $k = -6 \rightarrow 6$   
 $l = -18 \rightarrow 18$

*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<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.26$  e Å<sup>-3</sup>

*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<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 ( $\text{\AA}$ ,  $^\circ$ )

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 <sup>i</sup>	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 <sup>i</sup>	121.7 (5)
C2—C3—S1	109.6 (4)	C9—C10—C10 <sup>i</sup>	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 <sup>i</sup>	-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 <sup>i</sup> —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, °)*

<i>D—H···A</i>	<i>D—H</i>	<i>H···A</i>	<i>D···A</i>	<i>D—H···A</i>
N2—H2···N1 <sup>ii</sup>	0.86	1.93	2.790 (6)	178

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