

S,S'-(Pyridazine-3,6-diyl)dithiuronium dichloride methanol monosolvate

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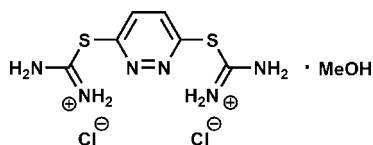
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.030; wR factor = 0.075; data-to-parameter ratio = 16.1.

In the title compound, $\text{C}_6\text{H}_{10}\text{N}_6\text{S}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{CH}_3\text{OH}$, the pyridazine ring is almost planar, the greatest deviation from the mean plane being 0.025 (2) Å for one of the ring N atoms. The two thiuronium substituents are tilted out of this plane by 60.87 (6) and 57.94 (7)°. The thiuronium cations and the chloride anions are linked by strong N—H...Cl hydrogen bonds. The methanol solvent molecule interacts with both the chloride ion (through an O—H...Cl hydrogen bond) and the cation (through an N—H...O hydrogen bond), resulting in a three-dimensional supramolecular arrangement.

Related literature

For pharmacological applications of pyridazine derivatives, see: Cignarella & Barlocco (2002). For details of the preparation, see: Kumagai (1960); Steck & Brundage (1959).



Experimental

Crystal data

$\text{C}_6\text{H}_{10}\text{N}_6\text{S}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{CH}_4\text{O}$
 $M_r = 333.26$
 Triclinic, $P\bar{1}$
 $a = 6.7457$ (2) Å
 $b = 9.0234$ (3) Å
 $c = 13.0165$ (4) Å

$\alpha = 104.148$ (2)°
 $\beta = 98.066$ (2)°
 $\gamma = 108.695$ (2)°
 $V = 706.81$ (4) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.75$ mm⁻¹
 $T = 293$ K

0.45 × 0.10 × 0.05 mm

Data collection

Stoe IPDS 2 diffractometer
 Absorption correction: integration
 (*X-RED*; Stoe & Cie, 2002)
 $T_{\min} = 0.739$, $T_{\max} = 0.959$

3234 measured reflections
 3234 independent reflections
 2765 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.075$
 $S = 1.03$
 3234 reflections
 201 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1G—H1G...Cl1 ⁱ	0.89 (3)	2.22 (3)	3.1038 (15)	171 (3)
N3—H3A...Cl2	0.92 (3)	2.28 (3)	3.1746 (17)	166 (2)
N3—H3B...O1G	0.89 (3)	1.95 (3)	2.839 (2)	171 (3)
N4—H4A...Cl1	0.86 (3)	2.70 (3)	3.3950 (16)	139 (2)
N4—H4B...Cl1 ⁱ	0.91 (3)	2.36 (3)	3.2522 (15)	167 (2)
N5—H5A...Cl1	0.89 (2)	2.39 (2)	3.2614 (16)	170 (2)
N5—H5B...Cl2 ⁱⁱ	0.90 (3)	2.25 (3)	3.1413 (17)	173 (2)
N6—H6A...Cl2 ⁱⁱⁱ	0.83 (3)	2.36 (3)	3.1878 (19)	175 (3)
N6—H6B...O1G ^{iv}	0.90 (3)	2.17 (2)	2.891 (2)	136 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2416).

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supplementary materials

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***S,S'*-(Pyridazine-3,6-diyl)dithiuronium dichloride methanol monosolvate**

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Comment

Pyridazine derivatives are important compounds for pharmacological applications, among them 3,6-dithiopyridazine being a secondary substance of the title compound (Cignarella & Barlocco, 2002).

In the title compound (Fig. 1), the pyridazine ring is almost planar, with maximal deviation from the mean plane 0.025 (2) Å. Dihedral angles between the pyridazine plane and thiourea substitutes are different (S2 C6 N5 N6 - 60.87 (6)° and S1 C5 N3 N4 - 57.94 (7)°).

The structure is formed by a (C₆H₁₀N₆S₂)²⁺ cation and two Cl⁻ anions, connected through strong N—H⋯Cl⁻ hydrogen bonds [H3A⋯Cl2 = 2.28 (3) Å, N3—H3A⋯Cl2 = 166 (2)°; H4A⋯Cl1 = 2.70 (3) Å, N4—H4A⋯Cl1 = 139 (2)°; H5A⋯Cl1 = 2.39 (3) Å, N5—H5A⋯Cl1 = 170 (2)°], and one solvate CH₃OH molecule bonded to the anion through a hydrogen bond [H3B⋯O1G = 2.839 (2) Å, N3—H3B⋯O1G = 171 (3)°]. Intermolecular hydrogen bonds link the Cl⁻ anions and the solvate MeOH molecule to two additional cations (Table 1) resulting in a three-dimensional supramolecular arrangement (Fig.2).

Experimental

The title compound has been obtained as an intermediate substance of the synthesis of 3,6-dithiopyridazine involving the reaction of 3,6-dichloropyridazine with thiourea in methanol solution and was isolated before alkaline treatment (Steck & Brundage, 1959); (Kumagai, 1960). The colourless plate-type single crystals are stable in the air.

Refinement

All H-atoms, except H-atoms involved in H-bonding, were positioned geometrically and allowed to ride on their parent atoms, with C—H=0.95 Å and $U_{\text{iso}} = 1.2\text{--}1.5 U_{\text{eq}}$ (parent atom). The rest H-atoms were located in a difference map and fully refined

Figures

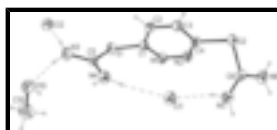


Fig. 1. Perspective view of the title compound, showing 50% probability displacement ellipsoids for the non-H atoms. Dashed lines represent hydrogen bond.

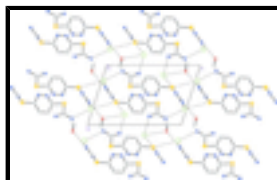


Fig. 2. Packing diagram of the title compound viewed down the *a* axis. The weak hydrogen bonds are shown as dashed lines. H-atoms are omitted for clarity

supplementary materials

{Amino[(6-{[amino(iminiumyl)methyl]sulfanyl}pyridazin-3-yl)sulfanyl]methylidene}azanium dichloride methanol monosolvate

Crystal data

$C_6H_{10}N_6S_2^{2+} \cdot 2Cl^- \cdot CH_4O$	$Z = 2$
$M_r = 333.26$	$F(000) = 344$
Triclinic, $P\bar{1}$	$D_x = 1.566 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 6.7457 (2) \text{ \AA}$	Cell parameters from 32534 reflections
$b = 9.0234 (3) \text{ \AA}$	$\theta = 1.7\text{--}29.6^\circ$
$c = 13.0165 (4) \text{ \AA}$	$\mu = 0.75 \text{ mm}^{-1}$
$\alpha = 104.148 (2)^\circ$	$T = 293 \text{ K}$
$\beta = 98.066 (2)^\circ$	Plate, colourless
$\gamma = 108.695 (2)^\circ$	$0.45 \times 0.10 \times 0.05 \text{ mm}$
$V = 706.81 (4) \text{ \AA}^3$	

Data collection

Stoe IPDS 2 diffractometer	3234 independent reflections
Radiation source: sealed X-ray tube, long-fine focus plane graphite	2765 reflections with $I > 2\sigma(I)$
Detector resolution: $6.67 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.071$
rotation method scans	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.5^\circ$
Absorption correction: integration (<i>X-RED</i> ; Stoe & Cie, 2002)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.739$, $T_{\text{max}} = 0.959$	$k = -11 \rightarrow 11$
3234 measured reflections	$l = 0 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.075$	$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.1092P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
3234 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
201 parameters	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: $0.055 (4)$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.46287 (7)	0.17255 (5)	0.64021 (3)	0.03256 (12)
C12	0.10144 (7)	0.26455 (6)	0.02016 (4)	0.03622 (12)
O1G	0.5002 (2)	-0.10500 (17)	0.13659 (11)	0.0364 (3)
C1G	0.7040 (4)	0.0147 (3)	0.1460 (2)	0.0570 (6)
H1G1	0.7251	0.1146	0.2013	0.085*
H1G2	0.7098	0.0358	0.0775	0.085*
H1G3	0.8152	-0.0251	0.1658	0.085*
H1G	0.518 (5)	-0.132 (4)	0.197 (2)	0.059 (8)*
H4B	0.434 (4)	0.053 (3)	0.357 (2)	0.048 (7)*
H5A	0.436 (4)	0.388 (3)	0.780 (2)	0.037 (6)*
H6B	0.410 (4)	0.684 (3)	0.992 (2)	0.040 (6)*
H3A	0.201 (4)	0.137 (3)	0.138 (2)	0.046 (6)*
H4A	0.441 (5)	0.205 (4)	0.439 (2)	0.059 (8)*
H5B	0.581 (4)	0.541 (3)	0.880 (2)	0.047 (7)*
H3B	0.330 (4)	0.032 (3)	0.169 (2)	0.056 (8)*
H6A	0.183 (5)	0.646 (3)	0.947 (2)	0.049 (7)*
S1	0.22215 (7)	0.35351 (5)	0.32279 (3)	0.02800 (11)
S2	0.02098 (7)	0.37603 (6)	0.77378 (3)	0.03286 (12)
C4	0.0693 (2)	0.36263 (19)	0.64195 (12)	0.0231 (3)
N1	0.2518 (2)	0.48701 (16)	0.53011 (11)	0.0265 (3)
N2	0.2047 (2)	0.49603 (17)	0.62795 (11)	0.0284 (3)
C3	-0.0424 (3)	0.2143 (2)	0.55821 (13)	0.0277 (3)
H3	-0.1409	0.1249	0.5703	0.033*
C1	0.1553 (2)	0.34686 (18)	0.44932 (12)	0.0220 (3)
N6	0.2904 (3)	0.6233 (2)	0.93770 (13)	0.0357 (3)
C6	0.2824 (3)	0.50356 (19)	0.85521 (13)	0.0261 (3)
C2	-0.0002 (3)	0.2071 (2)	0.45784 (13)	0.0271 (3)
H2	-0.0716	0.1135	0.3979	0.033*
N3	0.2723 (3)	0.1075 (2)	0.18987 (12)	0.0352 (3)
N5	0.4521 (3)	0.4721 (2)	0.83639 (13)	0.0335 (3)
N4	0.3980 (3)	0.1435 (2)	0.37169 (13)	0.0308 (3)
C5	0.3058 (2)	0.18519 (19)	0.29330 (13)	0.0232 (3)

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Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0377 (2)	0.0308 (2)	0.0310 (2)	0.01700 (17)	0.00766 (16)	0.00711 (15)
C12	0.0359 (2)	0.0417 (2)	0.0307 (2)	0.01407 (18)	0.00600 (16)	0.01193 (17)
O1G	0.0373 (7)	0.0351 (7)	0.0328 (7)	0.0125 (5)	0.0048 (5)	0.0066 (5)
C1G	0.0417 (12)	0.0504 (13)	0.0699 (16)	0.0099 (10)	0.0192 (11)	0.0091 (11)
S1	0.0392 (2)	0.0296 (2)	0.0249 (2)	0.02017 (17)	0.01270 (15)	0.01233 (15)
S2	0.0286 (2)	0.0409 (2)	0.02151 (19)	0.00569 (17)	0.00775 (15)	0.00506 (16)
C4	0.0239 (7)	0.0251 (7)	0.0206 (7)	0.0111 (6)	0.0049 (5)	0.0048 (6)
N1	0.0314 (7)	0.0223 (6)	0.0244 (6)	0.0086 (5)	0.0073 (5)	0.0064 (5)
N2	0.0342 (7)	0.0230 (6)	0.0238 (6)	0.0080 (5)	0.0072 (5)	0.0031 (5)
C3	0.0261 (7)	0.0244 (7)	0.0266 (8)	0.0038 (6)	0.0067 (6)	0.0050 (6)
C1	0.0227 (7)	0.0237 (7)	0.0213 (7)	0.0114 (6)	0.0048 (5)	0.0066 (5)
N6	0.0434 (9)	0.0308 (7)	0.0275 (7)	0.0142 (7)	0.0051 (7)	0.0009 (6)
C6	0.0317 (8)	0.0237 (7)	0.0216 (7)	0.0090 (6)	0.0048 (6)	0.0075 (6)
C2	0.0259 (7)	0.0240 (7)	0.0228 (7)	0.0042 (6)	0.0030 (6)	0.0003 (6)
N3	0.0454 (9)	0.0423 (8)	0.0237 (7)	0.0263 (7)	0.0087 (6)	0.0063 (6)
N5	0.0305 (8)	0.0345 (8)	0.0320 (7)	0.0130 (6)	0.0045 (6)	0.0044 (6)
N4	0.0393 (8)	0.0321 (7)	0.0255 (7)	0.0203 (6)	0.0062 (6)	0.0077 (6)
C5	0.0230 (7)	0.0230 (7)	0.0243 (7)	0.0081 (5)	0.0085 (5)	0.0074 (6)

Geometric parameters (\AA , $^\circ$)

O1G—C1G	1.417 (3)	C1—C2	1.398 (2)
O1G—H1G	0.89 (3)	N6—C6	1.305 (2)
C1G—H1G1	0.9600	N6—H6B	0.90 (3)
C1G—H1G2	0.9600	N6—H6A	0.83 (3)
C1G—H1G3	0.9600	C6—N5	1.305 (2)
S1—C5	1.7603 (16)	C2—H2	0.9300
S1—C1	1.7775 (15)	N3—C5	1.306 (2)
S2—C6	1.7709 (17)	N3—H3A	0.92 (3)
S2—C4	1.7738 (15)	N3—H3B	0.89 (3)
C4—N2	1.329 (2)	N5—H5A	0.89 (2)
C4—C3	1.399 (2)	N5—H5B	0.90 (3)
N1—C1	1.326 (2)	N4—C5	1.315 (2)
N1—N2	1.3450 (19)	N4—H4B	0.91 (3)
C3—C2	1.366 (2)	N4—H4A	0.86 (3)
C3—H3	0.9300		
C1G—O1G—H1G	103.6 (19)	C6—N6—H6A	122.6 (19)
O1G—C1G—H1G1	109.5	H6B—N6—H6A	114 (2)
O1G—C1G—H1G2	109.5	N6—C6—N5	123.12 (17)
H1G1—C1G—H1G2	109.5	N6—C6—S2	115.38 (14)
O1G—C1G—H1G3	109.5	N5—C6—S2	121.38 (13)
H1G1—C1G—H1G3	109.5	C3—C2—C1	116.94 (14)
H1G2—C1G—H1G3	109.5	C3—C2—H2	121.5
C5—S1—C1	100.19 (7)	C1—C2—H2	121.5

C6—S2—C4	99.98 (8)	C5—N3—H3A	120.2 (16)
N2—C4—C3	123.90 (14)	C5—N3—H3B	120.0 (18)
N2—C4—S2	117.88 (11)	H3A—N3—H3B	120 (2)
C3—C4—S2	118.18 (12)	C6—N5—H5A	119.1 (15)
C1—N1—N2	118.93 (13)	C6—N5—H5B	117.8 (16)
C4—N2—N1	119.05 (13)	H5A—N5—H5B	123 (2)
C2—C3—C4	116.86 (15)	C5—N4—H4B	121.2 (17)
C2—C3—H3	121.6	C5—N4—H4A	122 (2)
C4—C3—H3	121.6	H4B—N4—H4A	116 (3)
N1—C1—C2	124.05 (14)	N3—C5—N4	123.08 (15)
N1—C1—S1	114.57 (11)	N3—C5—S1	115.75 (13)
C2—C1—S1	121.20 (12)	N4—C5—S1	121.17 (12)
C6—N6—H6B	123.2 (15)		
C6—S2—C4—N2	-37.51 (14)	C5—S1—C1—N1	126.26 (12)
C6—S2—C4—C3	144.58 (13)	C5—S1—C1—C2	-58.54 (14)
C3—C4—N2—N1	-5.3 (2)	C4—S2—C6—N6	134.58 (13)
S2—C4—N2—N1	176.96 (11)	C4—S2—C6—N5	-49.21 (15)
C1—N1—N2—C4	2.6 (2)	C4—C3—C2—C1	1.9 (2)
N2—C4—C3—C2	2.9 (2)	N1—C1—C2—C3	-4.5 (2)
S2—C4—C3—C2	-179.32 (13)	S1—C1—C2—C3	-179.24 (12)
N2—N1—C1—C2	2.3 (2)	C1—S1—C5—N3	149.37 (13)
N2—N1—C1—S1	177.35 (11)	C1—S1—C5—N4	-31.32 (15)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1G—H1G \cdots C11 ⁱ	0.89 (3)	2.22 (3)	3.1038 (15)	171 (3)
N3—H3A \cdots C12	0.92 (3)	2.28 (3)	3.1746 (17)	166 (2)
N3—H3B \cdots O1G	0.89 (3)	1.95 (3)	2.839 (2)	171 (3)
N4—H4A \cdots C11	0.86 (3)	2.70 (3)	3.3950 (16)	139 (2)
N4—H4B \cdots C11 ⁱ	0.91 (3)	2.36 (3)	3.2522 (15)	167 (2)
N5—H5A \cdots C11	0.89 (2)	2.39 (2)	3.2614 (16)	170 (2)
N5—H5B \cdots C12 ⁱⁱ	0.90 (3)	2.25 (3)	3.1413 (17)	173 (2)
N6—H6A \cdots C12 ⁱⁱⁱ	0.83 (3)	2.36 (3)	3.1878 (19)	175 (3)
N6—H6B \cdots O1G ^{iv}	0.90 (3)	2.17 (2)	2.891 (2)	136 (2)

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

Fig. 1

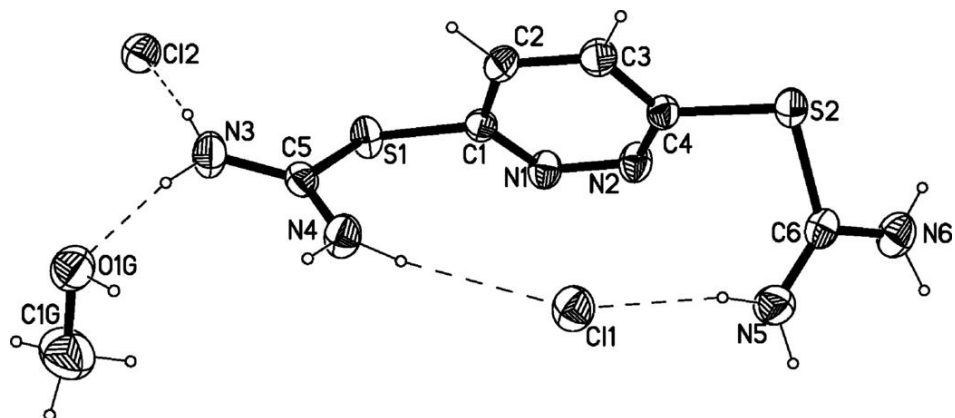


Fig. 2

