

# Crystal structure of dichloridobis(*N,N'*-dimethylthiourea- $\kappa$ S)mercury(II)

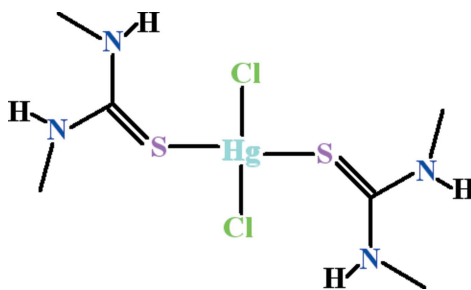
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The molecular structure of the title compound,  $[\text{HgCl}_2(\text{C}_3\text{H}_8\text{N}_2\text{S})_2]$ , has point group symmetry 2, with the twofold rotation axis passing through the  $\text{Hg}^{\text{II}}$  atom. The latter is coordinated by two Cl atoms and two *N,N'*-dimethylthiourea (Dmtu) ligands through their S atoms, defining a distorted tetrahedral coordination sphere with bond angles in the range 102.47 (4)–118.32 (4)°. Intra- and intermolecular hydrogen bonds of the type  $\text{N}-\text{H}\cdots\text{Cl}$  with  $S(6)$  and  $R_2^2(12)$  ring motifs are present. The intermolecular contacts make up polymeric chains extending parallel to [101].

## 1. Chemical context

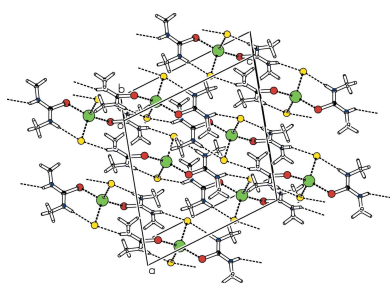
X-ray structural studies of mercury(II) complexes with thiourea ligands (*L*) or derivatives thereof have shown that in combination with a halide or pseudohalide *X*, some of the complexes exist as mononuclear species  $[\text{HgX}_2\text{L}_2]$  (Popović *et al.*, 2000), while the others exist in a dimeric or polymeric form as  $[\text{HgX}_2\text{L}]_n$  (Bell *et al.*, 2001) in the solid state. In both types of complexes, monomeric (1:2) or polymeric (1:1), the coordination environment around  $\text{Hg}^{\text{II}}$  is distorted tetrahedral or pseudo-tetrahedral. We have recently reported the crystal structures of  $\text{HgCl}_2$  and  $\text{Hg}(\text{CN})_2$  complexes with methylthiourea as an auxiliary ligand (Isab *et al.*, 2011), *N,N'*-dimethylthiourea (Malik *et al.*, 2010*a*), *N,N'*-diethylthiourea (Mufakkar *et al.*, 2010), *N,N'*-dibutylthiourea (Ahmad *et al.*, 2009) and tetramethylthiourea (Nawaz *et al.*, 2010).

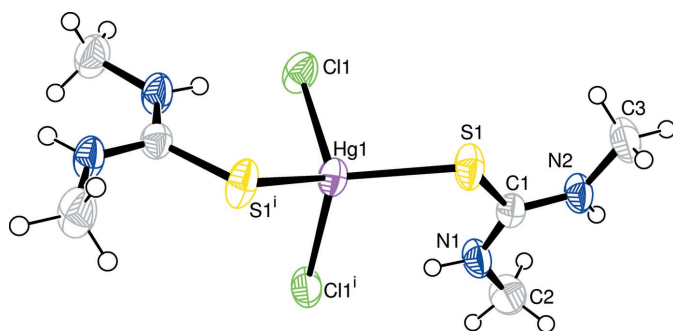


In this article, we report on synthesis and crystal structure of  $\text{HgCl}_2$  with dimethylthiourea (Dmtu) as an additional ligand,  $[\text{HgCl}_2(\text{C}_3\text{H}_8\text{N}_2\text{S})_2]$ , (I).

## 2. Structural comments

The mercury atom in complex (I) lies on a twofold rotation axis (Fig. 1). It exhibits a distorted tetrahedral coordination



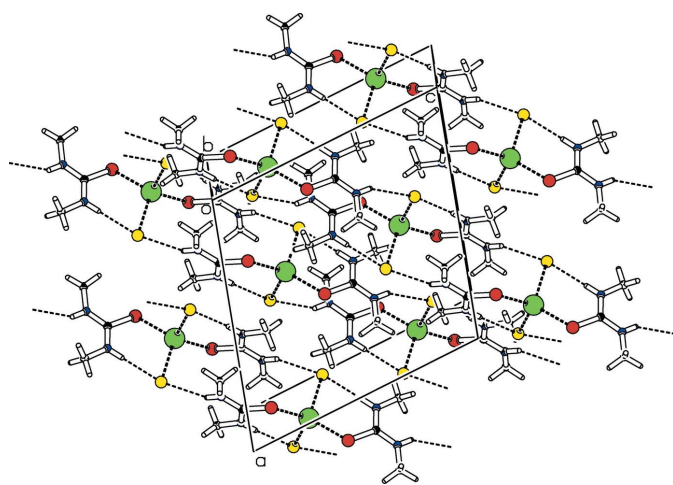

**Figure 1**

The molecular structure of compound (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radius. [Symmetry code: (i)  $-x + 1, y, -z + \frac{3}{2}$ ]

environment defined by two S atoms of symmetry-related Dmtu ligands and two Cl atoms. The S—Hg—S bond angle is  $118.32(4)^\circ$ . At  $102.47(4)^\circ$ , the Cl—Hg—Cl bond angle is significantly smaller, which can be attributed to the bulkier Dmtu ligands. The Hg—S, Hg—Cl and other bond lengths (Table 1) have similar values compared with other  $[\text{HgCl}_2\text{L}_2]$  complexes (Ahmad *et al.*, 2009; Isab *et al.*, 2011; Malik *et al.*, 2010a; Mufakkar *et al.*, 2010; Popović *et al.*, 2000). In (I), the N—(C=S)—N skeleton of the Dmtu ligand is essentially planar with an r.m.s. deviation of  $0.0135 \text{ \AA}$ .

### 3. Supramolecular features

From a supramolecular point of view, adjacent molecules are connected by intermolecular  $\text{N2—H2} \cdots \text{Cl1}$  hydrogen bonds (Table 2, Fig. 2) into  $R_2^2(12)$  ring motifs (Bernstein *et al.*, 1995). The supramolecular chains formed this way extend parallel to [010]. Additional intramolecular hydrogen bonds  $\text{N1—H1} \cdots \text{Cl1}$  (Table 2) with  $S(6)$  loop motifs (Bernstein *et al.*, 1995) are also present.


**Figure 2**

Crystal packing of compound (I) viewed approximately along [010]. N—H $\cdots$ Cl hydrogen bonds are shown as dashed lines (see Table 2 for details).

**Table 1**

Selected bond lengths ( $\text{\AA}$ ).

Hg1—S1	2.4622 (7)	Hg1—Cl1	2.5589 (7)
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**Table 2**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
$\text{N1—H1}\cdots\text{Cl1}$	0.86	2.37	3.223 (3)	170
$\text{N2—H2}\cdots\text{Cl1}^i$	0.86	2.49	3.270 (3)	151

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

### 4. Database survey

A systematic search in the Cambridge Structural Database (Groom & Allen, 2014) revealed a total of 25 hits for mercury chloride complexes with thiourea ligands. The title compound is isotopic with the Zn and Cd analogues  $[\text{ZnCl}_2(\text{Dmtu})_2]$  (Burrows *et al.*, 2004) and  $[\text{CdCl}_2(\text{Dmtu})_2]$  (Malik *et al.*, 2010b) and with  $[\text{CdBr}_2(\text{Dmtu})_2]$  (Ahmad *et al.*, 2011). The  $\text{Hg}^{\text{II}}$  atom in the structure of (I) shows an equivalent degree of distortion from the tetrahedral configuration as the metals in  $[\text{Zn}(\text{Dmtu})_2\text{Cl}_2]$  and  $[\text{Hg}(\text{tetramethylthiourea})_2\text{Cl}_2]$  (Nawaz *et al.*, 2010) in which the bond angles at the metal atom vary from  $104.35(2)$  to  $113.30(2)^\circ$  and from  $104.08(4)$  to  $120.75(4)^\circ$ , respectively. However, in  $[\text{CdCl}_2(\text{Dmtu})_2]$  and  $[\text{CdBr}_2(\text{Dmtu})_2]$ , the coordination spheres around Cd deviate only slightly from ideal tetrahedral values. On the other hand

**Table 3**

Experimental details.

Crystal data	
Chemical formula	$[\text{HgCl}_2(\text{C}_3\text{H}_8\text{NS})_2]$
$M_r$	479.84
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	296
$a, b, c$ ( $\text{\AA}$ )	13.1434 (12), 8.9971 (3), 12.6596 (9)
$\beta$ ( $^\circ$ )	107.955 (4)
$V$ ( $\text{\AA}^3$ )	1424.12 (17)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	11.45
Crystal size (mm)	$0.36 \times 0.18 \times 0.16$
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2007)
$T_{\text{min}}, T_{\text{max}}$	0.106, 0.265
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	12262, 1721, 1556
$R_{\text{int}}$	0.031
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.018, 0.038, 1.06
No. of reflections	1721
No. of parameters	71
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.42, $-0.32$

Computer programs: APEX2 and SAINT (Bruker, 2007), SHELXS97 (Sheldrick, 2008), SHELXL2014/6 (Sheldrick, 2015), ORTEP-3 for Windows and WinGX (Farrugia, 2012) and PLATON (Spek, 2009).

in  $[\text{Hg}(\text{Dmtu})_2(\text{CN})_2]$ , the  $\text{Hg}^{\text{II}}$  atom exhibits a severely distorted tetrahedral coordination sphere with bond angles in the range 94.31 (2) to 148.83 (13) $^\circ$  (Malik *et al.*, 2010a).

## 5. Synthesis and crystallization

For the preparation of title complex, 0.27 g (1 mmol)  $\text{HgCl}_2$  dissolved in 4 ml dimethylsulfoxide were mixed with two equivalents of *N,N'*-dimethylthiourea in 10 ml acetonitrile. After stirring for 15 minutes, the resulting solution was filtered and the filtrate kept at room temperature. After one day colourless crystals were obtained. Yield *ca.* 60%.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were positioned geometrically (C–H = 0.96 Å, N–H = 0.86 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ .

## Acknowledgements

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## supporting information

*Acta Cryst.* (2015). E71, 1061-1063 [doi:10.1107/S2056989015015406]

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### Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *S SAINT* (Bruker, 2007); data reduction: *S SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/6* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

### Dichloridobis(*N,N'*-dimethylthiourea- $\kappa$ S)mercury(II)

#### Crystal data

[HgCl<sub>2</sub>(C<sub>3</sub>H<sub>8</sub>NS)<sub>2</sub>]  
 $M_r = 479.84$   
 Monoclinic, *C2/c*  
 $a = 13.1434$  (12) Å  
 $b = 8.9971$  (3) Å  
 $c = 12.6596$  (9) Å  
 $\beta = 107.955$  (4)°  
 $V = 1424.12$  (17) Å<sup>3</sup>  
 $Z = 4$

$F(000) = 904$   
 $D_x = 2.238$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 1556 reflections  
 $\theta = 3.0$ – $28.0$ °  
 $\mu = 11.45$  mm<sup>-1</sup>  
 $T = 296$  K  
 Lath, colourless  
 $0.36 \times 0.18 \times 0.16$  mm

#### Data collection

Bruker Kappa APEXII CCD  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 Detector resolution: 7.50 pixels mm<sup>-1</sup>  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2007)  
 $T_{\min} = 0.106$ ,  $T_{\max} = 0.265$

12262 measured reflections  
 1721 independent reflections  
 1556 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$   
 $\theta_{\max} = 28.0$ °,  $\theta_{\min} = 3.0$ °  
 $h = -16 \rightarrow 17$   
 $k = -11 \rightarrow 11$   
 $l = -16 \rightarrow 16$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.038$   
 $S = 1.06$   
 1721 reflections  
 71 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 0.595P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.42$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.31$  e Å<sup>-3</sup>

*Special details*

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Hg1	0.5000	0.37748 (2)	0.7500	0.04175 (6)
Cl1	0.60610 (6)	0.19941 (10)	0.66623 (6)	0.05387 (19)
S1	0.36846 (7)	0.51777 (8)	0.60297 (6)	0.04873 (19)
N1	0.40138 (19)	0.3089 (3)	0.4670 (2)	0.0464 (6)
H1	0.4588	0.2910	0.5206	0.056*
N2	0.24749 (19)	0.4417 (3)	0.4042 (2)	0.0433 (5)
H2	0.2332	0.3894	0.3446	0.052*
C1	0.3374 (2)	0.4131 (3)	0.4824 (2)	0.0362 (6)
C2	0.3824 (3)	0.2226 (4)	0.3672 (3)	0.0553 (8)
H2A	0.4381	0.1500	0.3772	0.083*
H2B	0.3819	0.2870	0.3066	0.083*
H2C	0.3146	0.1732	0.3513	0.083*
C3	0.1704 (3)	0.5533 (4)	0.4096 (3)	0.0580 (9)
H3A	0.1572	0.5471	0.4800	0.087*
H3B	0.1048	0.5371	0.3509	0.087*
H3C	0.1978	0.6501	0.4015	0.087*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Hg1	0.04156 (10)	0.04908 (9)	0.02828 (9)	0.000	0.00146 (7)	0.000
Cl1	0.0503 (4)	0.0684 (5)	0.0368 (4)	0.0220 (4)	0.0044 (3)	-0.0017 (3)
S1	0.0591 (5)	0.0440 (4)	0.0315 (4)	0.0151 (3)	-0.0031 (3)	-0.0054 (3)
N1	0.0395 (14)	0.0570 (14)	0.0344 (13)	0.0126 (11)	-0.0007 (11)	-0.0056 (11)
N2	0.0425 (14)	0.0480 (12)	0.0308 (12)	0.0096 (11)	-0.0011 (11)	-0.0027 (11)
C1	0.0366 (16)	0.0375 (13)	0.0314 (14)	0.0001 (10)	0.0059 (12)	0.0026 (10)
C2	0.056 (2)	0.0626 (19)	0.0429 (18)	0.0096 (15)	0.0091 (16)	-0.0154 (15)
C3	0.051 (2)	0.067 (2)	0.0443 (19)	0.0258 (17)	-0.0017 (15)	-0.0002 (16)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Hg1—S1	2.4622 (7)	N2—C3	1.444 (4)
Hg1—S1 <sup>i</sup>	2.4622 (7)	N2—H2	0.8600
Hg1—Cl1	2.5589 (7)	C2—H2A	0.9600
Hg1—Cl1 <sup>i</sup>	2.5589 (7)	C2—H2B	0.9600
S1—C1	1.732 (3)	C2—H2C	0.9600

N1—C1	1.313 (4)	C3—H3A	0.9600
N1—C2	1.438 (4)	C3—H3B	0.9600
N1—H1	0.8600	C3—H3C	0.9600
N2—C1	1.312 (4)		
S1—Hg1—S1 <sup>i</sup>	118.32 (4)	N2—C1—S1	118.1 (2)
S1—Hg1—Cl1	110.67 (2)	N1—C1—S1	122.1 (2)
S1 <sup>i</sup> —Hg1—Cl1	106.79 (3)	N1—C2—H2A	109.5
S1—Hg1—Cl1 <sup>i</sup>	106.79 (3)	N1—C2—H2B	109.5
S1 <sup>i</sup> —Hg1—Cl1 <sup>i</sup>	110.67 (2)	H2A—C2—H2B	109.5
Cl1—Hg1—Cl1 <sup>i</sup>	102.47 (4)	N1—C2—H2C	109.5
C1—S1—Hg1	107.88 (9)	H2A—C2—H2C	109.5
C1—N1—C2	124.8 (3)	H2B—C2—H2C	109.5
C1—N1—H1	117.6	N2—C3—H3A	109.5
C2—N1—H1	117.6	N2—C3—H3B	109.5
C1—N2—C3	125.7 (3)	H3A—C3—H3B	109.5
C1—N2—H2	117.2	N2—C3—H3C	109.5
C3—N2—H2	117.2	H3A—C3—H3C	109.5
N2—C1—N1	119.8 (3)	H3B—C3—H3C	109.5
C3—N2—C1—N1	-179.5 (3)	C2—N1—C1—S1	-177.2 (2)
C3—N2—C1—S1	-0.5 (4)	Hg1—S1—C1—N2	159.3 (2)
C2—N1—C1—N2	1.8 (5)	Hg1—S1—C1—N1	-21.6 (3)

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

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ Cl1	0.86	2.37	3.223 (3)	170
N2—H2 $\cdots$ Cl1 <sup>ii</sup>	0.86	2.49	3.270 (3)	151

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