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# Dichlorobis(1,3-dimethylthiourea-$\kappa S$)zinc(II)

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Determination of the crystal structure of the title compound, $[ZnCl_2(C_3H_6N_2S)_2]$, reveals a distorted tetrahedral geometry around the zinc centre which occupies a twofold axis. Both intra- and intermolecular hydrogen bonding is observed between the 1,3-dimethylthiourea NH groups and the coordinated Cl atoms.

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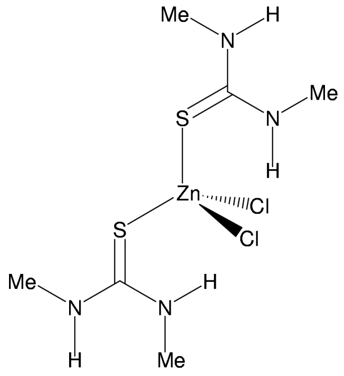
**Key indicators**

Single-crystal X-ray study
*T* = 150 K
Mean $\sigma$(N–C) = 0.003 Å
*R* factor = 0.028
*wR* factor = 0.067
Data-to-parameter ratio = 18.6

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

## Comment

The title compound, (I), was formed as part of our investigations into the formation of bis-thiourea zinc(II) dicarboxylate polymers (Burrows *et al.*, 2000, 2004; Burke *et al.*, 2003).



(I)

The asymmetric unit of (I) (Fig. 1) consists of a zinc(II) centre occupying a twofold symmetry axis, to which is coordinated one 1,3-dimethylthiourea ligand, *via* the S atom, and one Cl$^-$. The complete molecule is generated by transformation through a twofold rotation axis, inherent in the space group. The geometry around the Zn centre is distorted tetrahedral, with bond angles ranging from 104.35 (3) to

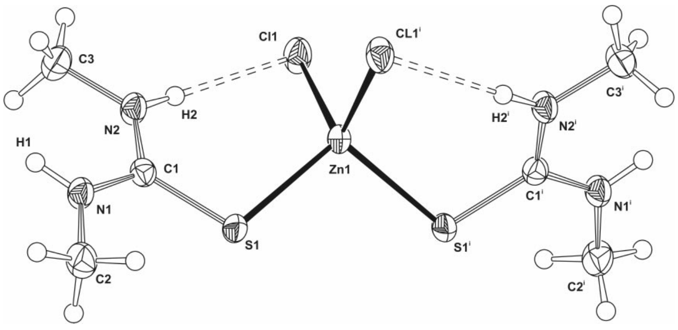


**Figure 1**
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms represented by small spheres. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

113.300 (19)°. This study confirms previous conclusions on the structure of (I) which emerged on the basis of IR studies (Marcotrigiano, 1975).

The NH groups of the 1,3-dimethylthiourea ligands are arranged such that they facilitate the formation of both intra- and intermolecular hydrogen bonds, involving $Cl^-$ anions as acceptors in both cases; details are given in Table 1. As seen in a number of zinc(II) bis(thiourea) dicarboxylate polymers (Burrows *et al.*, 2000), the intramolecular hydrogen bonds have graph-set notation $S(6)$. The intermolecular hydrogen bonds link the molecules into infinite hydrogen-bonded chains (Fig. 2). These interactions occur pairwise and lead to hydrogen-bonded rings with graph-set notation $R_2^2(12)$. There is no inter-chain hydrogen bonding present.

## Experimental

Equimolar aqueous solutions of zinc(II) tetra(1,3-dimethylthiourea) dichloride (Ashcroft, 1970) and sodium salts of succinic, itaconic or mesaconic acids were allowed to evaporate slowly over a period of two weeks, in each case resulting in the formation of colourless crystals. Analysis by single-crystal X-ray diffraction revealed the identity of the products as (I) and confirmed that the dicarboxylate was not incorporated into the structure.

### *Crystal data*

$[ZnCl_2(C_3H_6N_2S)_2]$
$M_r = 344.62$
Monoclinic, $C2/c$
$a = 13.0230\ (4)$ Å
$b = 8.9470\ (3)$ Å
$c = 12.4350\ (3)$ Å
$\beta = 106.967\ (2)°$
$V = 1385.82\ (7)$ Å$^3$
$Z = 4$
$D_x = 1.652$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1063 reflections
$\theta = 0.2–26.3°$
$\mu = 2.44$ mm$^{-1}$
$T = 150\ (2)$ K
Block, colourless
0.18 × 0.15 × 0.15 mm

### *Data collection*

Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.655$, $T_{max} = 0.697$
8273 measured reflections
1580 independent reflections
1439 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 16$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.067$
$S = 1.14$
1580 reflections
85 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0178P)^2 + 2.1477P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å$^{-3}$
$\Delta\rho_{min} = -0.44$ e Å$^{-3}$

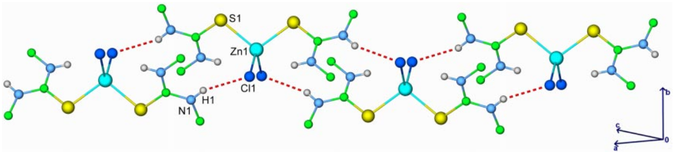


**Figure 2**
A view of the intermolecular hydrogen-bond interactions in (I), leading to chains along the crystallographic [101] direction.

**Table 1**
Hydrogen-bonding geometry (Å, °).

| $D-\mathrm{H}\cdots A$ | $D-\mathrm{H}$ | $\mathrm{H}\cdots A$ | $D\cdots A$ | $D-\mathrm{H}\cdots A$ |
|---|---|---|---|---|
| N2—H2···Cl1 | 0.884 (17) | 2.337 (18) | 3.2110 (19) | 170 (3) |
| N1—H1···Cl1$^{i}$ | 0.887 (17) | 2.47 (2) | 3.2737 (19) | 152 (2) |

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

H atoms were included at calculated positions on all carbon centres, being constrained to an ideal geometry with C—H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. Each group was allowed to rotate freely about its C—N bond. The position of the amino H atoms were located from the difference map and refined isotropically subject to a distance constraint of 0.89 Å.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL* and local programs.

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**m1318** Andrew D. Burrows *et al.* • $[ZnCl_2(C_3H_6N_2S)_2]$ *Acta Cryst.* (2004). E**60**, m1317–m1318

# supporting information

*Acta Cryst.* (2004). E**60**, m1317–m1318 [https://doi.org/10.1107/S1600536804020550]

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$Z = 4$
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Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å
Cell parameters from 25 reflections
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$\mu = 2.44$ mm$^{-1}$
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Block, colourless
0.18 × 0.15 × 0.15 mm

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Nonius KappaCCD area-detector diffractometer
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8273 measured reflections
1580 independent reflections
1439 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 27.5°$, $\theta_{min} = 4.0°$
$h = -16 \rightarrow 16$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.067$
$S = 1.14$
1580 reflections
85 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0178P)^2 + 2.1477P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å$^{-3}$
$\Delta\rho_{min} = -0.44$ 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 (Å²)*

| | $x$ | $y$ | $z$ | $U_{\rm iso}$*/$U_{\rm eq}$ |
|---|---|---|---|---|
| Zn1 | 0.5000 | 0.65085 (4) | 0.2500 | 0.02036 (12) |
| Cl1 | 0.39368 (4) | 0.80208 (7) | 0.32074 (4) | 0.03019 (15) |
| S1 | 0.60867 (4) | 0.49039 (6) | 0.38451 (4) | 0.02451 (15) |
| N1 | 0.74153 (14) | 0.5551 (2) | 0.58578 (15) | 0.0249 (4) |
| H1 | 0.760 (2) | 0.611 (3) | 0.6472 (19) | 0.043 (8)* |
| N2 | 0.59505 (15) | 0.7072 (2) | 0.52832 (15) | 0.0248 (4) |
| H2 | 0.5344 (16) | 0.730 (3) | 0.477 (2) | 0.034 (7)* |
| C1 | 0.65113 (16) | 0.5921 (2) | 0.50836 (17) | 0.0205 (4) |
| C2 | 0.8128 (2) | 0.4339 (3) | 0.5763 (2) | 0.0334 (5) |
| H2A | 0.8203 | 0.4326 | 0.5001 | 0.043 (8)* |
| H2C | 0.7827 | 0.3385 | 0.5914 | 0.052 (9)* |
| H2B | 0.8834 | 0.4490 | 0.6309 | 0.054 (9)* |
| C3 | 0.62235 (19) | 0.7902 (3) | 0.63317 (19) | 0.0302 (5) |
| H3A | 0.6953 | 0.8301 | 0.6488 | 0.022 (6)* |
| H3B | 0.6185 | 0.7237 | 0.6945 | 0.043 (8)* |
| H3C | 0.5716 | 0.8730 | 0.6270 | 0.042 (8)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.02062 (19) | 0.02289 (19) | 0.01535 (18) | 0.000 | 0.00177 (13) | 0.000 |
| Cl1 | 0.0290 (3) | 0.0365 (3) | 0.0220 (3) | 0.0119 (2) | 0.0026 (2) | −0.0025 (2) |
| S1 | 0.0288 (3) | 0.0223 (3) | 0.0178 (3) | 0.0039 (2) | −0.0006 (2) | −0.00186 (19) |
| N1 | 0.0237 (9) | 0.0275 (9) | 0.0198 (9) | 0.0034 (7) | 0.0005 (7) | −0.0016 (7) |
| N2 | 0.0226 (9) | 0.0285 (10) | 0.0196 (9) | 0.0047 (7) | 0.0002 (7) | −0.0026 (7) |
| C1 | 0.0200 (10) | 0.0223 (10) | 0.0187 (9) | −0.0023 (8) | 0.0047 (8) | 0.0015 (8) |
| C2 | 0.0321 (12) | 0.0357 (13) | 0.0277 (11) | 0.0124 (10) | 0.0016 (9) | 0.0000 (10) |
| C3 | 0.0304 (12) | 0.0328 (12) | 0.0256 (12) | 0.0019 (10) | 0.0051 (9) | −0.0072 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—Cl1 | 2.2874 (6) | N2—C1 | 1.327 (3) |
| Zn1—Cl1$^{i}$ | 2.2874 (6) | N2—C3 | 1.452 (3) |
| Zn1—S1 | 2.3410 (5) | C2—H2A | 0.9800 |
| Zn1—S1$^{i}$ | 2.3410 (5) | C2—H2C | 0.9800 |
| S1—C1 | 1.734 (2) | C2—H2B | 0.9800 |
| N1—H1 | 0.887 (17) | C3—H3A | 0.9800 |
| N1—C1 | 1.327 (3) | C3—H3B | 0.9800 |
| N1—C2 | 1.454 (3) | C3—H3C | 0.9800 |
| N2—H2 | 0.884 (17) | | |

| | | | |
|---|---|---|---|
| Cl1—Zn1—Cl1$^{i}$ | 107.47 (3) | S1—C1—N2 | 121.53 (15) |
| Cl1—Zn1—S1 | 113.300 (19) | N1—C1—N2 | 118.55 (19) |
| Cl1$^{i}$—Zn1—S1$^{i}$ | 113.300 (19) | N1—C2—H2A | 109.5 |
| Cl1—Zn1—S1$^{i}$ | 109.27 (2) | N1—C2—H2C | 109.5 |
| Cl1$^{i}$—Zn1—S1 | 109.27 (2) | N1—C2—H2B | 109.5 |
| S1—Zn1—S1$^{i}$ | 104.35 (3) | H2A—C2—H2C | 109.5 |
| Zn1—S1—C1 | 106.40 (7) | H2A—C2—H2B | 109.5 |
| H1—N1—C1 | 116.6 (19) | H2C—C2—H2B | 109.5 |
| H1—N1—C2 | 118.0 (19) | N2—C3—H3A | 109.5 |
| C1—N1—C2 | 125.39 (19) | N2—C3—H3B | 109.5 |
| H2—N2—C1 | 117.8 (18) | N2—C3—H3C | 109.5 |
| H2—N2—C3 | 117.8 (18) | H3A—C3—H3B | 109.5 |
| C1—N2—C3 | 124.14 (18) | H3A—C3—H3C | 109.5 |
| S1—C1—N1 | 119.92 (16) | H3B—C3—H3C | 109.5 |

| | | | |
|---|---|---|---|
| Cl1—Zn1—S1—C1 | −38.29 (8) | C3—N2—C1—S1 | 175.64 (17) |
| Cl1$^{i}$—Zn1—S1—C1 | 81.50 (7) | C3—N2—C1—N1 | −4.3 (3) |
| S1$^{i}$—Zn1—S1—C1 | −157.04 (8) | Zn1—S1—C1—N1 | −155.05 (15) |
| C2—N1—C1—S1 | 1.1 (3) | Zn1—S1—C1—N2 | 25.05 (19) |
| C2—N1—C1—N2 | −179.0 (2) | | |

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

### *Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···Cl1 | 0.88 (2) | 2.34 (2) | 3.2110 (19) | 170 (3) |
| N1—H1···Cl1$^{ii}$ | 0.89 (2) | 2.47 (2) | 3.2737 (19) | 152 (2) |

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