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## Structure of Dichlorobis(1,3-thiazolidine-2-thione-S)zinc(II)

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**Abstract.**  $[\text{ZnCl}_2(\text{C}_3\text{H}_5\text{NS}_2)_2]$ ,  $M_r = 374.7$ , monoclinic,  $P2_1/n$ ,  $a = 8.773$  (3),  $b = 11.274$  (3),  $c = 13.877$  (4) Å,  $\beta = 99.44$  (3)°,  $U = 1353.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.82$  (2),  $D_x = 1.84$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 2.81$  mm<sup>-1</sup>,  $F(000) = 752$ ,  $T = 293$  K, final  $R = 0.038$  for 2486 observed reflections. The Zn atom is tetrahedrally coordinated by two 1,3-thiazolidine-2-thione ligands and two Cl atoms. The ligands are bonded through the thione S atom to the metal with Zn–S 2.361 (1) and 2.369 (1) Å. The crystal structure is stabilized by intra- and intermolecular N–H...Cl hydrogen bonds.

**Introduction.** Compounds like 1,3-thiazolidine-2-thione (ttz), containing a secondary thioamide group, are of considerable interest as ligands since they are found to provide potential binding sites for metal ions in many physiological systems (Raper, 1985). The ttz ligand is also of great interest in the chemistry of coordination compounds since it can act either as a neutral molecule or as a deprotonated anion, possessing in both forms more than one donor atom (Raper, Oughtred & Nowell, 1983).

Our crystallographic studies of the Pd<sup>II</sup> (Kubiak & Głowiak, 1982) and Cd<sup>II</sup> (Kubiak & Głowiak, 1985) complexes have shown that ttz is S-bonded to the metal. To check the possibilities of metal–N bond formation by ttz (Preti & Tosi, 1976) we have studied also the interaction of Zn<sup>II</sup> with this ligand and the X-ray structure of such a system is presented here.

**Experimental.** Clear colourless crystals from zinc(II) chloride and ttz, at room temperature (293 K), dimensions 0.3 × 0.3 × 0.4 mm;  $D_m$  by flotation in carbon tetrachloride/ethylene bromide; monoclinic from Weissenberg photographs,  $P2_1/n$ ; Syntex  $P2_1$

computer-controlled four-circle diffractometer, scintillation counter, Mo  $K\alpha$  radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections; 3132 independent reflections; variable  $\theta/2\theta$  scan, scan rate 2.0–29.3° min<sup>-1</sup> (depending on intensity),  $2\theta_{\text{max}} = 55.0^\circ$ ; two standards measured every 30 reflections, no significant change; correction for Lorentz and polarization effects, not for absorption; 2486 reflections with  $F > 6\sigma(F)$  used for structure determination; index range  $h$  0–11,  $k$  0–14,  $l$  –18–17; calculations performed on a Nova 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); heavy-atom method, full-matrix least squares (on  $F$ ); non-H atoms refined with anisotropic and H atoms with fixed positional and one overall isotropic thermal parameter ( $B = 4.8$  Å<sup>2</sup>), 136 variables;  $(\Delta/\sigma)_{\text{max}} = 0.1$ ;  $\Delta\rho_{\text{max}} = \pm 0.5$  e Å<sup>-3</sup>;  $R = 0.038$ ,  $wR = 0.046$ ,  $S = 3.70$ ,  $w = 1/\sigma^2(F)$ .

**Discussion.** Final atomic parameters are given in Table 1\* and interatomic distances and selected angles in Table 2. A view of the complex and the atom-numbering scheme is shown in Fig. 1. Fig. 2 is a stereoscopic view of the molecular packing.

The ttz ligands are monodentate and S-bonded to the Zn<sup>II</sup> ion is coordinated in a tetrahedral manner to two thiazolidine-2-thione ligands and two Cl atoms.

\* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, bond angles, least-squares-plane calculations and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43503 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses

	$B_{eq} = \frac{1}{3} \sum_i B_{ii}$			$B_{eq} (\text{\AA}^2)$
	x	y	z	
Zn	0.27300 (6)	0.21514 (5)	0.06995 (4)	2.71 (3)
Cl(1)	0.2693 (1)	0.1871 (1)	-0.0919 (1)	3.4 (1)
Cl(2)	0.1922 (1)	0.3985 (1)	0.1063 (1)	4.0 (1)
S(1)	0.0981 (1)	0.0848 (1)	0.1282 (1)	3.3 (1)
S(2)	0.3550 (1)	-0.0840 (1)	0.0996 (1)	4.5 (1)
S(3)	0.5345 (1)	0.1827 (1)	0.1401 (1)	3.2 (1)
S(4)	0.8193 (1)	0.3246 (1)	0.1473 (1)	3.2 (1)
N(1)	0.0931 (4)	-0.1494 (4)	0.1351 (3)	3.0 (3)
N(2)	0.5606 (4)	0.4205 (4)	0.1582 (3)	3.4 (3)
C(1)	0.1711 (5)	-0.0537 (4)	0.1220 (3)	2.7 (3)
C(2)	0.3365 (6)	-0.2411 (5)	0.1227 (4)	3.6 (4)
C(3)	0.1642 (6)	-0.2639 (5)	0.1216 (4)	3.7 (4)
C(4)	0.6221 (5)	0.3174 (4)	0.1486 (3)	2.6 (3)
C(5)	0.8228 (6)	0.4838 (5)	0.1628 (5)	4.4 (5)
C(6)	0.6601 (7)	0.5226 (5)	0.1651 (6)	6.5 (7)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Zn—Cl(1)	2.264 (1)	Cl(1)—Zn—Cl(2)	113.16 (5)
Zn—Cl(2)	2.269 (1)	Cl(1)—Zn—S(1)	110.40 (5)
Zn—S(1)	2.361 (1)	Cl(1)—Zn—S(3)	104.00 (5)
Zn—S(3)	2.369 (1)	Cl(2)—Zn—S(1)	104.29 (5)
		Cl(2)—Zn—S(3)	111.47 (5)
		S(1)—Zn—S(3)	113.77 (5)
Zn—S(1)—C(1)	106.50 (16)	Zn—S(3)—C(4)	106.70 (16)
C(1)—S(1)	1.694 (5)	C(4)—S(3)	1.697 (5)
C(1)—S(2)	1.727 (5)	C(4)—S(4)	1.735 (5)
C(1)—N(1)	1.306 (6)	C(4)—N(2)	1.297 (6)
S(2)—C(2)	1.812 (5)	S(4)—C(5)	1.807 (6)
N(1)—C(3)	1.459 (7)	N(2)—C(6)	1.439 (7)
C(2)—C(3)	1.531 (7)	C(5)—C(6)	1.498 (9)

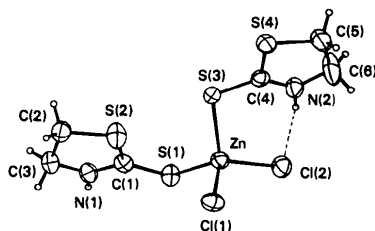


Fig. 1. A view of the complex showing the atom-numbering scheme.

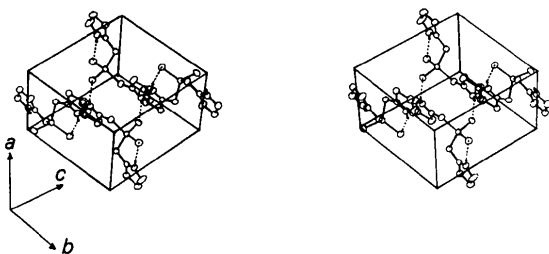


Fig. 2. A stereoscopic view showing the molecular packing.

The Zn coordination sphere is somewhat distorted from tetrahedral as the Cl(1)—Zn—Cl(2) [113.16 (5) $^\circ$ ] and S(1)—Zn—S(3) [113.77 (5) $^\circ$ ] angles indicate (Table 2). The angle between the ZnCl(1)S(3) and ZnCl(2)S(1) planes is 88.1 (1) $^\circ$ .\*

The ttz ligands are monodentate and S-bonded to the metal. The same behaviour is found in tetrakis(1,3-thiazolidine-2-thione)palladium(II) dichloride-1,3-thiazolidine-2-thione (Kubiak & Głowiak, 1982) and in *catena*-poly[(1,3-thiazolidine-2-thione)cadmium]- $\mu$ -chloro- $\mu_3$ -chloro (Kubiak & Głowiak, 1985). The Zn—S distances [2.361 (1) and 2.369 (1)  $\text{\AA}$ ] are comparable to the sum of the Zn and S tetrahedral covalent radii, 2.35  $\text{\AA}$  (Pauling, 1960) and to the values found in other tetrahedral Zn compounds (Nowell, Cox & Raper, 1979). The Zn—S—C angles [106.50 (16) and 106.70 (16) $^\circ$ ] and the torsion angles Zn—S—C—N [−169.7 (4) and 28.1 (5) $^\circ$ ] and Zn—S—C—S [11.1 (3) and −153.3 (3) $^\circ$ ] indicate that the S atom is largely  $sp^3$  in character (Spofford & Amma, 1976; Raper & Nowell, 1979).

The bond lengths and angles in the ttz ligands have not been appreciably affected by the bonding with Zn. Only the coordinated C—S bonds [1.694 (5) and 1.697 (5)  $\text{\AA}$ ] are a little longer than in the free state [1.671 (7) and 1.680 (7)  $\text{\AA}$  (Raper *et al.*, 1983)]. One 4,5-dihydrothiazole ring has a slightly deformed half-chair conformation with deviations from the least-squares plane through S(2)C(1)N(1) of −0.202 (5) and 0.106 (5)  $\text{\AA}$  for C(2) and C(3), respectively,  $\{\Delta C_{\frac{1}{2}}^{(C(2), C(3))} = 1.5^\circ$  (Duax, Weeks & Rohrer, 1976)}. The second ring is essentially planar, the largest deviation from the ring plane being 0.020 (8)  $\text{\AA}$  for C(6). The thione atoms, S(1) and S(3), are out of these planes by −0.018 (1) and −0.043 (1)  $\text{\AA}$ , respectively.

An interesting feature of the crystal structure is the intramolecular hydrogen bond between N(2) and Cl(2) [N(2)⋯Cl(2) 3.203 (4)  $\text{\AA}$ , N(2)—H⋯Cl(2) 154 $^\circ$ ]. There is also an intermolecular hydrogen bond between Cl(1) and N(1)(−x, −y, −z) [N(1)⋯Cl(1)(−x, −y, −z) 3.166 (4)  $\text{\AA}$ , N(1)—H⋯Cl(1)(−x, −y, −z) 141 $^\circ$ ].

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\* See deposition footnote.

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## Structure of Dimeric Dibromo(di-2-pyridylmethane)copper(II)

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**Abstract.**  $[\text{CuBr}_2(\text{C}_{11}\text{H}_{10}\text{N}_2)]_2$ ,  $M_r = 787.14$ , monoclinic,  $P2_1/n$ ,  $a = 8.988$  (8),  $b = 13.933$  (8),  $c = 9.795$  (6) Å,  $\beta = 98.54$  (4)°,  $V = 1213$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.16$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 8.332$  mm<sup>-1</sup>,  $F(000) = 756$ ,  $T = 291$  K,  $R = 0.053$  for 1621 unique observed reflections. The crystal consists of well defined dimeric units linked by two Cu–Br bonds. The coordination polyhedron around the Cu atom can be described as a distorted square pyramid. The basal plane is formed by the two N atoms of the di-2-pyridylmethane ligand and two Br atoms. The axial site is occupied by a Br atom from the other monomeric unit. Cu–N(1) = 2.027 (5), Cu–N(2) = 2.016 (5), Cu–Br(1) = 2.488 (1) and Cu–Br(2) = 2.391 (1) Å compared to the axial bond Cu–Br(1') = 2.804 (1) Å; Cu...Cu' = 3.869 (1) Å.

**Introduction.** The present work continues investigations on the structure of dimeric complexes of copper(II) (Garland, Le Marouille & Spodine, 1985). The recent interest in binuclear copper complexes is due to their potential as models for metalloproteins. A considerable number of complexes have been prepared with two metal ions at a separation of 2.5–6.0 Å. The variation of the metal–metal distance and the nature of the donor atoms allow the study of spectroscopic and magnetic properties that depend on the binuclearity of the system (Karlin & Zubieta, 1983). The structures of a number

of halogen-bridged compounds have been investigated in the hope of correlating their structural and magnetic properties (Marsh, Bowman, Hatfield & Hodgson, 1982; Wilson, Hatfield & Hodgson, 1976).

**Experimental.** The complex was prepared by addition of 1 mmol of anhydrous CuBr<sub>2</sub> to a degassed solution containing 1 mmol of ligand in freshly distilled methanol. The resultant solution was refluxed under N<sub>2</sub>. Dark-green crystals formed when the reaction mixture was cooled.

Crystal dimensions: 0.12 × 0.20 × 0.33 mm, Nonius CAD-4  $\kappa$ -geometry diffractometer, cell dimensions calculated by least-squares refinement on setting angles of 25 reflections with  $12.2 \leq 2\theta \leq 20.6^\circ$ ; 2262 integrated reflections collected up to  $(\sin\theta)/\lambda = 0.595$  Å<sup>-1</sup>;  $\omega$ -2 $\theta$ -scan technique, scan width  $(1.0 + 0.35 \tan\theta)^\circ$ ;  $0 < h < 10$ ,  $0 < k < 16$ ,  $-11 < l < 11$ ; 0.6% decay in intensities of three standard reflections during 31 h of irradiation; no absorption correction and no time-decay corrections applied; 2004 unique reflections after averaging ( $R_{\text{int}} = 0.025$ ); 1621 with  $F^2 > 3\sigma(F^2)$ ; structure solution by MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refined by full-matrix least squares based on  $F_o$ , weights based on counting statistics:  $1/w = \sigma^2(F) = \frac{1}{4}\{[\sigma^2(I) + (0.08I)^2]/I\}$  (Stout & Jensen, 1968); atomic scattering factors for neutral atoms from *International*