

## Structure of 2-(2-Thioxo-1,3-thiazolidin-3-yl)-4,5-dihydro-1,3-thiazolium Aquatrichlorozincate(II)

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**Abstract.**  $[\text{C}_6\text{H}_9\text{N}_2\text{S}_3][\text{ZnCl}_3(\text{H}_2\text{O})]$ ,  $M_r = 395.1$ , triclinic,  $P\bar{1}$ ,  $a = 12.009$  (3),  $b = 12.632$  (2),  $c = 11.344$  (3) Å,  $\alpha = 115.16$  (4),  $\beta = 110.85$  (4),  $\gamma = 83.04$  (4)°,  $U = 1454.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.80$  (2),  $D_x = 1.80$  Mg m<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 2.67$  mm<sup>-1</sup>,  $F(000) = 792$ ,  $T = 293$  K, final  $R = 0.033$  for 2920 reflections. The unit cell contains two crystallographically independent  $\text{ZnCl}_3(\text{H}_2\text{O})^-$  anions and  $\text{C}_6\text{H}_9\text{N}_2\text{S}_3^+$  (4,5-dihydro-3-thiazoliumylthiazolidine-2-thione = ttztH<sup>+</sup>) cations. There is no direct bonding between the metal atom and the cation. The distorted  $\text{ZnCl}_3(\text{H}_2\text{O})^-$  anions are linked to the cations through hydrogen bonding involving H atoms attached to the thiazoliumyl N atom, with N...Cl distances 3.188 (6) and 3.242 (6) Å, and N–H...Cl angles 162 (6) and 165 (5)°.

**Introduction.** The 1,3-thiazolidine-2-thione (ttz) ligand is known to form complexes with transition metals, being coordinated through either the N of the ring or the exocyclic S of the thioketo group. Raper, Oughtred & Nowell (1983) recently reported the X-ray analysis of ttz with extensive data on the interaction of this ligand with various metals. Our crystallographic studies of the Pd (Kubiak & Głowiak, 1982) and Cd (Kubiak & Głowiak, 1985) complexes have shown that ttz is S bonded to the metal.

In the course of an investigation of the system  $\text{ZnCl}_2 + \text{ttz}$  with conc. HCl, we have noted the formation of a new, rather unexpected, compound of overall composition (dihydrothiazoliumylthiazolidine-2-thione)<sup>+</sup>. $\text{ZnCl}_3(\text{H}_2\text{O})^-$ .

Clark & Sykes (1971) prepared ttzt by treating 4,5-dihydro-1,3-thiazole-2-thiol with  $\text{H}_2\text{O}_2$  and suggested that it is probably formed by oxidation of the 2-thiol group of one molecule of the dihydrothiazole followed by nucleophilic attack by the N atom of a second molecule, with the oxygenated S atom acting as a good leaving group. The ttzt ligand is also one of the major products of the reaction of the thallium(I) salt of ttz with thiophosgene (Fujita, Nagao, Seno, Takao, Miyasaka, Kimura & Watson, 1981).

The X-ray investigation of the title compound was undertaken as part of our systematic studies of the

complexes of 1,3-thiazolidine-2-thione and its derivatives with divalent metals.

**Experimental.** Pale yellow crystals from  $\text{ZnCl}_2$  and ttz with conc. HCl obtained by slow evaporation at room temperature (293 K) from aqueous solution; dimensions 0.3 × 0.35 × 0.45 mm;  $D_m$  by flotation in carbon tetrachloride/ethylene bromide; triclinic from Weissenberg photographs,  $P\bar{1}$ ; Syntex  $P2_1$  computer-controlled four-circle diffractometer, scintillation counter,  $\text{Mo } K\alpha$  radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections; 3236 independent reflections; variable  $\theta$ – $2\theta$  scan, scan rate 2.0–29.3° min<sup>-1</sup> (depending on intensity),  $2\theta_{\text{max}} = 45^\circ$ , two standards measured every 30 reflections, no significant change; correction for Lorentz and polarization effects, not for absorption; 2920 reflections with  $F > 8\sigma(F)$  used for structure determination; index range  $h$  0→12,  $k$  –13→13,  $l$  –12→11; calculations performed on 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 water and imino H atoms with isotropic temperature factors; remaining H atoms with fixed positional and thermal parameters;  $(\Delta/\sigma)_{\text{max}} = 0.1$ ;  $\Delta\rho$  within –0.3 and 0.25 e Å<sup>-3</sup>;  $R = 0.033$ ,  $w = 1/\sigma^2(F)$ ,  $wR = 0.035$ ,  $S = 2.65$ .

**Discussion.** Tables 1 and 2 contain the atomic coordinates, thermal parameters and intramolecular bonding parameters.\* Fig. 1 shows the atomic numbering.

The asymmetric unit consists of two  $\text{ZnCl}_3(\text{H}_2\text{O})^-$  anions and two dihydrothiazoliumylthiazolidine-2-thione cations. The ttztH<sup>+</sup> cations do not participate in coordination to the metal ion, but form ionic and hydrogen-bonded contacts with  $\text{ZnCl}_3(\text{H}_2\text{O})^-$  ions. As

\* Lists of structure factors, anisotropic thermal parameters, calculated H-atom parameters and H-bond parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42578 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

shown in Table 2, the coordination geometry of the ZnCl<sub>3</sub>(H<sub>2</sub>O)<sup>-</sup> anion is distorted tetrahedral. The Zn—Cl and Zn—H<sub>2</sub>O distances are 2.218 to 2.240 (2) Å, and 2.019 and 2.035 (2) Å, respectively, while L—Zn—L angles within the coordination polyhedra range from 99.4 (1) to 115.0 (1)°.

The dihydrothiazoliumylthiazolidine-2-thione cations can be formally considered to be derived by linking a thiazolidine-2-thione ring and a 4,5-dihydro-1,3-thiazole ring *via* the C—N bond, as shown in Fig. 1. The dihydrothiazolyl N atom is a protonation site, which is confirmed by refinement of the H atoms bonded to N(12) and N(22).

There are no significant differences between the bond lengths and angles of the two crystallographically independent ttztH<sup>+</sup> cations. The molecular parameters for the dihydrothiazolyl ring are very similar to those reported for 1,3-thiazolidine-2-thione (Raper *et al.*, 1983). In contrast, in the N-substituted thiazolidine-2-thione moiety significant shortening of C—S<sub>exo</sub> and lengthening of C<sub>sp<sup>2</sup></sub>—N bond distances are observed.

Thus the thione bond lengths, 1.624 (6) and 1.638 (6) Å, are longer than the value expected for a double bond (1.61 Å; Pauling, 1960), but are shorter

than the 1.671 and 1.680 (7) Å given by Raper *et al.* (1983) for the ttz ligand. The lengthened bonds C(11)—N(11), 1.394 (8) Å, and C(21)—N(21), 1.396 (8) Å, are similar to the 1.390 (7) Å obtained for the N-substituted amide of 1,3-thiazolidine-2-thione (Fujita *et al.*, 1981).

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Zn(1)—Cl(1)	2.225 (2)	Zn(2)—Cl(4)	2.232 (2)
Zn(1)—Cl(2)	2.220 (2)	Zn(2)—Cl(5)	2.218 (2)
Zn(1)—Cl(3)	2.240 (2)	Zn(2)—Cl(6)	2.237 (2)
Zn(1)—W(1)	2.035 (5)	Zn(2)—W(2)	2.019 (5)
C(11)—S(11)	1.624 (6)	C(21)—S(21)	1.638 (6)
C(11)—S(12)	1.721 (7)	C(21)—S(22)	1.703 (7)
C(11)—N(11)	1.394 (8)	C(21)—N(21)	1.396 (8)
S(12)—C(12)	1.777 (8)	S(22)—C(22)	1.801 (7)
N(11)—C(13)	1.481 (8)	N(21)—C(23)	1.480 (8)
N(11)—C(14)	1.347 (8)	N(21)—C(24)	1.341 (8)
C(12)—C(13)	1.480 (11)	C(22)—C(23)	1.510 (10)
C(14)—S(13)	1.735 (6)	C(24)—S(23)	1.740 (6)
C(14)—N(12)	1.310 (8)	C(24)—N(22)	1.310 (8)
N(12)—C(16)	1.466 (10)	N(22)—C(26)	1.462 (10)
S(13)—C(15)	1.826 (8)	S(23)—C(25)	1.820 (8)
C(15)—C(16)	1.454 (11)	C(25)—C(26)	1.477 (11)
Cl(1)—Zn(1)—Cl(2)	115.0 (1)	Cl(4)—Zn(2)—Cl(5)	114.7 (1)
Cl(1)—Zn(1)—Cl(3)	112.8 (1)	Cl(4)—Zn(2)—Cl(6)	113.3 (1)
Cl(1)—Zn(1)—W(1)	104.5 (1)	Cl(4)—Zn(2)—W(2)	107.8 (2)
Cl(2)—Zn(1)—Cl(3)	114.9 (1)	Cl(5)—Zn(2)—Cl(6)	113.3 (1)
Cl(2)—Zn(1)—W(1)	108.2 (1)	Cl(5)—Zn(2)—W(2)	102.6 (2)
Cl(3)—Zn(1)—W(1)	99.4 (1)	Cl(6)—Zn(2)—W(2)	103.8 (2)
S(11)—C(11)—S(12)	121.5 (4)	S(21)—C(21)—S(22)	121.3 (4)
S(11)—C(11)—N(11)	127.8 (5)	S(21)—C(21)—N(21)	126.3 (5)
S(12)—C(11)—N(11)	110.7 (4)	S(22)—C(21)—N(21)	112.3 (4)
S(12)—C(12)—C(13)	109.0 (5)	S(22)—C(22)—C(23)	107.7 (5)
N(11)—C(13)—C(12)	109.5 (6)	N(21)—C(23)—C(22)	109.8 (5)
C(11)—S(12)—C(12)	95.1 (3)	C(21)—S(22)—C(22)	95.1 (3)
C(11)—N(11)—C(13)	115.6 (5)	C(21)—N(21)—C(23)	115.0 (5)
C(11)—N(11)—C(14)	125.5 (5)	C(21)—N(21)—C(24)	126.4 (5)
C(13)—N(11)—C(14)	118.9 (5)	C(23)—N(21)—C(24)	118.6 (5)
N(11)—C(14)—N(12)	121.2 (5)	N(21)—C(24)—N(22)	121.1 (5)
N(11)—C(14)—S(13)	125.0 (4)	N(21)—C(24)—S(23)	125.2 (5)
S(13)—C(14)—N(12)	113.8 (4)	S(23)—C(24)—N(22)	113.7 (5)
C(14)—S(13)—C(15)	90.3 (3)	C(24)—S(23)—C(25)	91.0 (3)
C(14)—N(12)—C(16)	116.9 (6)	C(24)—N(22)—C(26)	117.3 (6)
N(12)—C(16)—C(15)	107.9 (6)	N(22)—C(26)—C(25)	108.3 (6)
S(13)—C(15)—C(16)	109.5 (6)	S(23)—C(25)—C(26)	109.2 (5)

Table 1. Positional parameters and isotropic temperature factors (Å<sup>2</sup>) with *e.s.d.*'s in parentheses

For non-hydrogen atoms  $B_{eq} = \frac{1}{3} \sum B_{ii}$ ; for H atoms  $B_{iso}$  is the refined isotropic temperature factor.

	x	y	z	$B_{eq}/B_{iso}$
Zn(1)	0.00183 (6)	0.24736 (6)	0.39807 (7)	3.07 (5)
Zn(2)	0.47042 (6)	0.24064 (5)	0.57806 (7)	2.98 (5)
Cl(1)	-0.0787 (2)	0.1276 (1)	0.4460 (2)	5.4 (1)
Cl(2)	0.1115 (1)	0.1613 (1)	0.2633 (2)	4.7 (1)
Cl(3)	-0.1277 (1)	0.3744 (1)	0.3385 (2)	4.4 (1)
Cl(4)	0.3716 (1)	0.3150 (1)	0.7277 (2)	4.2 (1)
Cl(5)	0.4953 (2)	0.3609 (1)	0.4922 (2)	6.1 (2)
Cl(6)	0.6378 (1)	0.1542 (1)	0.6536 (2)	4.1 (1)
S(11)	0.1964 (2)	0.4388 (1)	-0.0444 (2)	5.4 (2)
S(12)	0.2346 (2)	0.3802 (1)	0.1895 (2)	5.0 (1)
S(13)	0.1040 (1)	0.6778 (1)	0.0073 (2)	4.1 (1)
S(21)	0.2790 (2)	0.0393 (2)	0.0364 (2)	6.3 (2)
S(22)	0.3137 (1)	0.1159 (1)	-0.1571 (2)	4.5 (1)
S(23)	0.3591 (1)	-0.2028 (1)	-0.0105 (2)	4.2 (1)
W(1)	0.1100 (4)	0.3598 (4)	0.5857 (4)	3.8 (4)
W(2)	0.3681 (5)	0.1088 (4)	0.4083 (5)	4.1 (4)
N(11)	0.1496 (4)	0.5773 (4)	0.1908 (4)	2.9 (4)
N(12)	0.0708 (4)	0.7615 (4)	0.2407 (5)	3.6 (4)
N(21)	0.3685 (4)	-0.0912 (4)	-0.1680 (4)	3.1 (4)
N(22)	0.4353 (4)	-0.2792 (4)	-0.2156 (5)	3.9 (4)
C(11)	0.1899 (5)	0.4740 (5)	0.1082 (6)	3.3 (5)
C(12)	0.1962 (7)	0.4731 (6)	0.3376 (7)	6.6 (7)
C(13)	0.1526 (6)	0.5840 (5)	0.3254 (6)	4.6 (6)
C(14)	0.1090 (4)	0.6686 (5)	0.1574 (5)	2.8 (4)
C(15)	0.0566 (7)	0.8286 (6)	0.0709 (7)	6.1 (7)
C(16)	0.0261 (6)	0.8549 (6)	0.1933 (8)	5.9 (7)
C(21)	0.3219 (5)	0.0128 (5)	-0.0951 (6)	3.5 (5)
C(22)	0.3687 (6)	0.0240 (5)	-0.2952 (7)	5.0 (6)
C(23)	0.3970 (5)	-0.0924 (5)	-0.2851 (6)	4.3 (5)
C(24)	0.3893 (4)	-0.1869 (5)	-0.1412 (5)	2.9 (4)
C(25)	0.4058 (6)	-0.3536 (6)	-0.0675 (7)	5.3 (6)
C(26)	0.4564 (6)	-0.3787 (6)	-0.1774 (8)	6.7 (7)
H(1W1)	0.097 (6)	0.436 (6)	0.603 (7)	6.6 (20)
H(2W1)	0.186 (6)	0.330 (6)	0.597 (7)	7.0 (20)
H(1W2)	0.379 (5)	0.040 (6)	0.399 (6)	4.9 (18)
H(2W2)	0.295 (8)	0.133 (8)	0.391 (9)	11.4 (32)
H(N12)	0.065 (6)	0.780 (6)	0.332 (7)	7.6 (20)
H(N22)	0.451 (5)	-0.289 (5)	-0.293 (6)	4.0 (14)

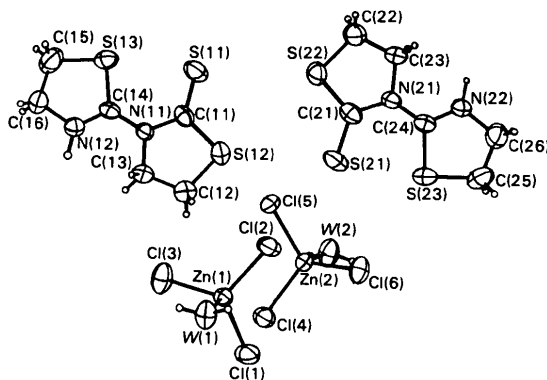


Fig. 1. View of the two independent cations and anions showing the atom numbering.

The five-membered rings in each molecule are slightly different in conformation. In cation 1 the thiazolidine ring adopts a flattened envelope conformation with C(12) 0.054 (8) Å out of the four-atom plane while the dihydrothiazolyl ring has a twist conformation with C(15) and C(16) deviating by -0.157 (9) and 0.054 (8) Å from the S(13)C(14)-N(12) plane. In cation 2 both five-membered rings have flattened pseudo half-chair conformations (Table 3). The torsion angles,  $-1.0(6)^\circ$  for C(13)-N(11)-C(14)-N(12),  $-2.6(5)^\circ$  for C(11)-N(11)-C(14)-S(13) and  $0.8(7)^\circ$  for C(23)-N(21)-C(24)-N(22),  $1.5(6)^\circ$  for C(21)-N(21)-C(24)-S(23), indicate that these fragments are essentially coplanar.

The orientations of the heterocyclic rings around the inter-ring C-N bonds are such that the exocyclic S atom of the thiazolidinethione moiety and the endocyclic S atom of the dihydrothiazolyl ring are *cis* with intramolecular S...S distances 2.972 (3) and 2.971 (3) Å, respectively, in the two independent cations.

There are six hydrogen bonds, each having a Cl atom as acceptor (Table 4, deposited). All H atoms bonded to N and O participate in the hydrogen-bonding network.

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## Structure of Copper Zinc Cyclohexylenediaminetetraacetate Hexahydrate

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**Abstract.** Pentaquazinc(II) [*N,N,N',N'*-tetrakis-(carboxymethyl)-1,2-cyclohexanediaminato]cuprate(II) monohydrate,  $[\text{Zn}(\text{H}_2\text{O})_5][\text{Cu}(\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_8)] \cdot \text{H}_2\text{O}$ ,  $M_r = 579.3$ , orthorhombic, *Pbc*2<sub>1</sub>,  $a = 10.868(3)$ ,  $b = 11.139(8)$ ,  $c = 17.432(5)$  Å,  $V = 2110(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.823$  Mg m<sup>-3</sup>, *Mo Kα*,  $\lambda = 0.71069$  Å,  $\mu = 2.248$  mm<sup>-1</sup>,  $F(000) = 1196$ , room temperature,  $R = 0.030$ ,  $wR = 0.034$  for 1780 observed reflections

0108-2701/86/040421-05\$01.50

Table 3. *Least-squares planes*

Values are given in the following order: atoms defining the plane, equation of plane, deviations of atoms from the plane (Å) with e.s.d.'s in parentheses.

Plane 1:	S(12), N(11), C(11), C(13) $-0.8682X - 0.2533Y - 0.42672Z + 0.40657 = 0$ S(12) -0.000 (2), N(11) -0.002 (5), C(11) 0.003 (6), C(13) 0.003 (7), S(11) 0.019 (2), C(12) 0.054 (8), C(14) -0.006 (6), N(12) 0.014 (5)
Plane 2:	S(13), C(14), N(12) $-0.8567X - 0.2386Y - 0.4572Z + 3.9853 = 0$ C(15) -0.157 (9), C(16) 0.054 (8), N(11) -0.023 (5)
Plane 3:	C(22), C(23), N(21) $-0.7857X - 0.1026Y - 0.6101Z + 2.8675 = 0$ S(22) -0.024 (2), C(21) 0.015 (6), S(21) 0.055 (2), C(24) -0.019 (6)
Plane 4:	N(22), C(24), S(23) $-0.7696X - 0.1152Y - 0.6280Z + 2.7610 = 0$ C(25) 0.104 (7), C(26) -0.028 (8), N(21) 0.007 (5)
Interplanar angles (°):	
	1-2 2.0 (5)
	3-4 1.6 (6)

### References

- CLARK, A. D. & SYKES, P. (1971). *J. Chem. Soc. C*, pp. 103-110.  
 FUJITA, E., NAGAO, Y., SENO, K., TAKAO, S., MIYASAKA, T., KIMURA, M. & WATSON, W. H. (1981). *J. Chem. Soc. Perkin Trans 1*, pp. 914-919.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 KUBIAK, M. & GŁOWIAK, T. (1982). *Acta Cryst.* **B38**, 2031-2034.  
 KUBIAK, M. & GŁOWIAK, T. (1985). *Acta Cryst.* **C41**, 1580-1582.  
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., pp. 224-239. Ithaca: Cornell Univ. Press.  
 RAPER, E. S., OUGHTRED, R. E. & NOWELL, I. W. (1983). *Inorg. Chim. Acta*, **77**, L89-L93.  
 Syntax (1976). *XTL/XTLE Structure Determination System*. Syntax Analytical Instruments, Cupertino, California.

$[I > 2\sigma(I)]$ . The structure is characterized by dinuclear entities in which the two metal atoms are linked through a  $\mu(O,O')$ -type carboxylate bridge. The Cu atom is bound to two N atoms and to four O atoms from the *cdta* ligand in a tetragonally elongated octahedral environment. The Zn atom displays nearly regular octahedral coordination being bound to five water molecules and to an O atom from the bridging