O(11)	0.4533 (1)	0.2301 (1)	0.3422 (2)	0.041 (1)
O(12)	0.4089 (1)	0.2873 (1)	0.3620 (2)	0.045 (1)
O(21)	0.3142 (1)	0.1398 (1)	0.3327 (2)	0.048 (1)
O(22)	0.2592 (1)	0.1012 (1)	0.1978 (2)	0.060 (1)
N(11)	0.3143 (2)	0.2378 (2)	0.0199 (3)	0.052 (2)
N(12)	0.3314 (2)	0.2635 (2)	0.1816 (3)	0.051 (2)
N(21)	0.4422 (2)	0.0324 (2)	0.3356 (3)	0.052 (2)
N(22)	0.4642 (2)	0.1261 (2)	0.3940 (3)	0.059 (2)
C(1)	0.3442 (3)	0.2427 (2)	0.1019 (3)	0.036 (1)
C(2)	0.4408 (2)	0.0844 (2)	0.3244 (3)	0.043 (2)
C(11)	0.4519 (2)	0.2762 (1)	0.3781 (2)	0.037 (1)
C(12)	0.5050 (2)	0.3184 (2)	0.4426 (3)	0.057 (2)
C(13)	0.5582 (3)	0.3083 (3)	0.4440 (6)	0.115 (4)
C(21)	0.2629 (2)	0.1075 (2)	0.2882 (3)	0.046 (2)
C(22)	0.2063 (2)	0.0752 (3)	0.3522 (4)	0.093 (3)
C(23)	0.1489 (3)	0.0478 (4)	0.3107 (6)	0.112 (4)

Table 2. *Selected geometric parameters* (Å, °)

Zn—S(1)	2.320 (1)	Zn—S(2)	2.341 (2)
Zn—O(11)	1.988 (2)	Zn—O(21)	1.959 (3)
S(1)—C(1)	1.731 (5)	S(2)—C(2)	1.723 (4)
O(11)—C(11)	1.269 (5)	O(12)—C(11)	1.260 (6)
O(21)—C(21)	1.278 (4)	O(22)—C(21)	1.236 (5)
N(11)—C(1)	1.312 (5)	N(12)—C(1)	1.309 (6)
N(21)—C(2)	1.331 (7)	N(22)—C(2)	1.310 (5)
C(11)—C(12)	1.499 (5)	C(12)—C(13)	1.477 (10)
C(21)—C(22)	1.508 (6)	C(22)—C(23)	1.369 (8)
S(1)—Zn—S(2)	105.2 (1)	O(11)—Zn—O(21)	101.9 (1)
S(1)—Zn—O(11)	108.9 (1)	S(2)—Zn—O(11)	106.2 (1)
S(1)—Zn—O(21)	125.4 (1)	S(2)—Zn—O(21)	107.9 (1)
Zn—S(1)—C(1)	103.3 (1)	Zn—S(2)—C(2)	105.6 (2)
Zn—O(11)—C(11)	120.7 (3)	Zn—O(21)—C(21)	115.7 (2)
S(1)—C(1)—N(11)	118.3 (3)	S(1)—C(1)—N(12)	121.8 (3)
N(11)—C(1)—N(12)	119.9 (5)	N(21)—C(2)—N(22)	118.4 (4)
S(2)—C(2)—N(21)	117.7 (3)	S(2)—C(2)—N(22)	123.9 (4)
O(11)—C(11)—O(12)	123.3 (3)	O(21)—C(21)—O(22)	122.6 (3)
O(11)—C(11)—C(12)	116.7 (4)	O(21)—C(21)—C(22)	116.4 (3)
O(12)—C(11)—C(12)	120.0 (4)	O(22)—C(21)—C(22)	120.9 (3)
C(11)—C(12)—C(13)	116.3 (5)	C(21)—C(22)—C(23)	120.2 (5)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N22—H8···O22^{i}	0.90 (7)	1.92 (7)	2.802 (4)	168 (2)
N22—H7···O11	0.95 (6)	1.92 (6)	2.842 (4)	165 (3)
N11—H2···O12^{ii}	0.88 (7)	1.99 (7)	2.857 (5)	171 (2)
N12—H4···O12	0.77 (6)	2.23 (6)	2.996 (4)	172 (2)
N11—H1···O21^{iii}	0.86 (6)	2.15 (6)	2.997 (4)	167 (2)
N21—H6···O12^{iv}	0.85 (6)	2.23 (6)	3.028 (4)	156 (2)
N21—H5···O22^{i}	0.77 (6)	2.32 (7)	3.029 (5)	155 (2)

Symmetry codes: (i) $\frac{2}{3}+y-x, \frac{1}{3}-x, \frac{1}{3}+z$; (ii) $\frac{1}{3}+y-x, \frac{2}{3}-x, z-\frac{1}{3}$; (iii) $x, x-y, z-\frac{1}{2}$; (iv) $\frac{2}{3}-y, \frac{1}{3}-x, z-\frac{1}{6}$.

The structure was solved by heavy-atom methods and Fourier techniques and refined by blocked-cascade full-matrix least squares with anisotropic displacement parameters for all non-H atoms. The H atoms attached to C atoms were included at calculated positions with fixed bond lengths (0.96 Å) and constrained angles; displacement parameters were set at 0.080 Å^2. The H atoms of the amino groups were located from a $\Delta\rho$ map. The calculations were performed with the *SHELXTL-Plus* program package (Sheldrick 1990). The figures were drawn with the same package.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and hydrogen-bonding parameters have been deposited with the IUCr (Reference: AB1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(thiourea-κS)bis(trichloroacetato-κO)zinc(II) Monohydrate

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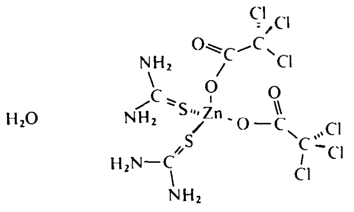
Abstract

The crystal structure of the complex [$Zn(C_2Cl_3O_2)_2(CH_4N_2S)_2$].$H_2O$ is reported. The structure consists of discrete molecules bridged by hydrogen bonds to form an infinite three-dimensional network. The first coordination sphere of the Zn atom is best described as a deformed tetrahedron composed of two Zn—O bonds [2.012 (5) and 2.000 (5) Å] and two Zn—S bonds [2.316 (2) and 2.291 (2) Å]. The distances from the Zn atom to the non-bonded carboxylate O atoms are beyond the normal bonding distance.

Comment

As part of our study on the synthesis, crystallochemistry, properties and biological activity of zinc carboxylates, either with or without additional ligands, the title complex, (I), was isolated and its crystal structure determined. The complex was prepared by mixing a freshly prepared suspension of zinc hydroxide with an aqueous solution of trichloroacetic acid and an aqueous solution of thiourea in a 1:2:2 molar ratio. After several days colourless needles of the title complex were filtered off, washed with water and ethanol and dried in air. The expected composition of the prepared crystals was confirmed by elemental analysis.



(I)

The title complex is molecular and is built up of $[Zn(thiourea)_2(Cl_3CCOO)_2]$ and H_2O molecules (Fig. 1). The uncoordinated water molecule links a carboxylate group with one amino group of the same molecule *via* an intramolecular hydrogen bond and one amino group of another molecule *via* an intermolecular hydrogen bond (Table 3).

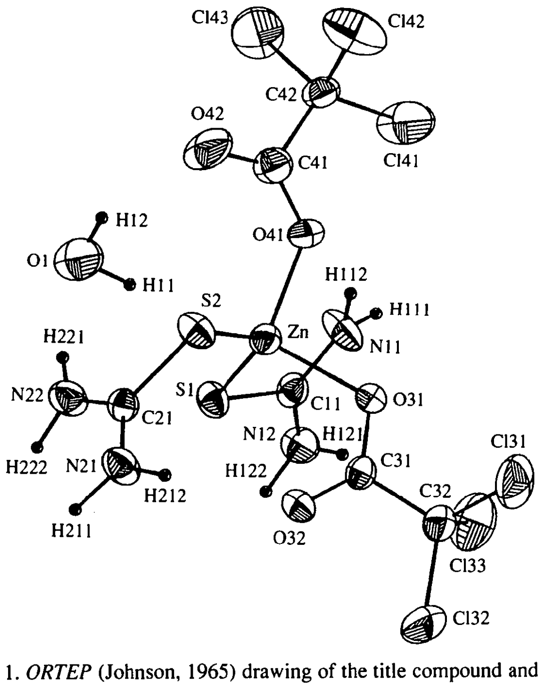


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound and the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The coordination polyhedron around the Zn atom is a deformed tetrahedron. The bond angles have close to ideal tetrahedral values with the exception of the S1—Zn—S2 angle [123.3 (1)°] (Table 2). The Zn—O bonds are somewhat longer than those found in similar complexes such as $[Zn(thiourea)_2(Ac)_2]$ [1.973 (6) and 1.954 (8) Å; Cavalca, Gasparri, Andreetti & Domiano, 1967] and the monoclinic form of $[Zn(Ac)_2]$ [in the range 1.949 (2)–1.965 (2) Å; Clegg, Little & Straughan, 1986]; this may be due to the strong electron-withdrawing effect of the three Cl atoms. On the other hand, the Zn—S bonds are within the range of Zn—S bond distances found in the $[Zn(thiourea)_2(Ac)_2]$ complex [2.326 (2)–2.261 (4) Å; Cavalca, Gasparri, Andreetti & Domiano, 1967].

The remaining two atoms from the carboxyl groups are at long distances from the Zn atom [2.915 (5) and 3.283 (7) Å]. Similar values were found in the analogous acetato complex [2.891 (9) and 2.996 (5) Å; Cavalca, Gasparri, Andreetti & Domiano, 1967]. The analogous distances are substantially shorter in the salicylato complex $[Zn(2\text{-}HOC_6H_4COO)_2(H_2O)_2]$ [2.523 (4) and 2.523 (4) Å; Rissanen, Valkonen, Kokkonen & Leskelä, 1987] and in the nitrobenzoate complex $[Zn(4\text{-}NO_2C_6H_4COO)_2(H_2O)_2]$ [2.522 (6) and 2.511 (6) Å; Gusejnov, Musaev, Amiraslanov, Usubaliev & Mamedov, 1983]. Only one weak Zn···O interaction was found in the complex $[Zn(4\text{-}H_2NC_6H_4COO)_2(H_2O)_{1.5}]$ [2.494 (8) Å; Amiraslanov, Nadzhafov, Usubaliev, Musaev, Movsumov & Mamedov, 1980], with the second Zn···O distance longer [3.395 (8) Å] than the distances found in the title trichloroacetato complex.

The trichloroacetate ions and the thiourea molecules are almost perfectly planar. The greatest distance of an atom from the least-square plane [0.016 (6) Å for the atom C21] was found in the second thiourea molecule, the remaining distances being smaller than 0.005 (6) Å.

Experimental

Crystal data

$[Zn(C_2Cl_3O_2)_2(CH_4N_2S)_2].H_2O$
$M_r = 560.39$
Monoclinic
$P2_1/c$
$a = 5.972\ (2)$ Å
$b = 23.103\ (11)$ Å
$c = 14.400\ (5)$ Å
$\beta = 102.91\ (3)°$
$V = 1937\ (1)$ Å^3
$Z = 4$
$D_x = 1.922$ Mg m^{-3}

Ag $K\alpha$ radiation
$\lambda = 0.56090$ Å
Cell parameters from 30 reflections
$\theta = 6.89–11.09°$
$\mu = 1.216$ mm^{-1}
$T = 293$ K
Needles
0.3 × 0.1 × 0.1 mm
White
Crystal source: crystallization from aqueous solution

Data collection

Hilger & Watts diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7245 measured reflections
3678 independent reflections
2429 observed reflections $[I_o > 3\sigma(I_o)]$

$R_{int} = 0.047$
$\theta_{max} = 20.0°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 28$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 30 reflections intensity variation: 5%

Refinement

Refinement on F
$R = 0.0578$

$(\Delta/\sigma)_{max} = 0.1$ (0.3 for water O atom)

$wR = 0.0570$
$S = 4.119$
2424 reflections
217 parameters
H-atom parameters not refined
$w = 4.178/\sigma^2(F)$

$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Zn	0.24633 (14)	0.13936 (3)	0.08967 (5)	0.0302 (2)
S1	0.6422 (3)	0.1490 (1)	0.1216 (1)	0.0339 (6)
C11	0.6999 (11)	0.1829 (3)	0.2325 (4)	0.0319 (13)
N11	0.5533 (10)	0.2179 (3)	0.2578 (4)	0.0482 (13)
N12	0.8970 (10)	0.1730 (3)	0.2902 (4)	0.0411 (13)
S2	0.0371 (3)	0.0960 (1)	−0.0451 (1)	0.0367 (6)
C21	0.2472 (11)	0.0558 (3)	−0.0826 (4)	0.0293 (13)
N21	0.2280 (10)	−0.0006 (2)	−0.0884 (4)	0.0421 (14)
N22	0.4172 (10)	0.0819 (3)	−0.1086 (5)	0.0434 (15)
O31	0.1963 (8)	0.0996 (2)	0.2077 (3)	0.0338 (13)
O32	0.3552 (8)	0.0219 (2)	0.1590 (3)	0.0413 (12)
C31	0.2811 (10)	0.0492 (3)	0.2168 (5)	0.0287 (15)
C32	0.2869 (12)	0.0217 (3)	0.3154 (5)	0.0404 (14)
Cl31	0.0137 (4)	0.0227 (1)	0.3414 (2)	0.0701 (8)
Cl32	0.3908 (8)	−0.0496 (1)	0.3222 (2)	0.0898 (10)
Cl33	0.4756 (4)	0.0636 (1)	0.4017 (2)	0.0749 (9)
O41	0.1347 (8)	0.2189 (2)	0.1109 (3)	0.0363 (12)
O42	0.0260 (13)	0.2525 (3)	−0.0361 (4)	0.0916 (14)
C41	0.0533 (12)	0.2560 (3)	0.0498 (5)	0.0421 (14)
C42	−0.0216 (11)	0.3141 (3)	0.0897 (5)	0.0376 (14)
Cl41	0.0587 (6)	0.3191 (1)	0.2131 (2)	0.0961 (9)
Cl42	−0.3253 (4)	0.3175 (1)	0.0568 (2)	0.0795 (10)
Cl43	0.0859 (5)	0.3722 (1)	0.0372 (2)	0.0782 (9)
O1	0.4433 (11)	0.2087 (2)	−0.0920 (4)	0.0673 (14)

Table 2. *Selected geometric parameters* (Å, °)

Zn—S1	2.316 (2)	Zn—O31	2.012 (5)
Zn—S2	2.291 (2)	Zn—O41	2.000 (5)
O31—Zn—O41	100.0 (2)	S1—Zn—O41	104.0 (2)
S2—Zn—O41	113.2 (2)	S1—Zn—O31	102.3 (1)
S2—Zn—O31	111.1 (2)	S1—Zn—S2	123.3 (1)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H112···O41	1.01 (1)	1.975 (4)	2.892 (7)	150 (4)
N22—H221···O1	0.90 (1)	2.058 (5)	2.940 (8)	166 (5)
O1—H11···S1	1.08 (1)	2.384 (2)	3.338 (6)	146 (3)
O1—H12···O42	0.97 (1)	2.125 (8)	2.963 (10)	143 (4)
N11—H111···O1^{i}	0.77 (1)	2.197 (6)	2.936 (9)	162 (5)
N12—H121···O42^{ii}	1.03 (1)	2.049 (6)	2.992 (9)	151 (4)
N12—H122···O31^{iii}	0.96 (1)	1.973 (5)	2.904 (8)	162 (4)
N21—H211···O32^{iv}	1.06 (1)	1.970 (5)	2.933 (8)	149 (3)
N22—H222···O32^{iv}	0.96 (1)	2.020 (5)	2.927 (8)	156 (4)

Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $1+x, y, z$; (iv) $1-x, -y, -z$.

Programs used to solve and refine the structure were *SDS* (Petříček & Malý, 1990) and *SHELX76* (Sheldrick, 1976). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from the final difference Fourier map and were not refined. Geometrical analysis was performed using *PARST* (Nardelli, 1983). *ORTEP* (Johnson, 1965) was employed for drawing the molecular structure.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including distances involving H atoms, have been deposited with the IUCr (Reference: KA1068). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trichloromethyltin(IV)

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Abstract

The crystal structure of trichloromethyltin(IV), $[SnCl_3(CH_3)]$, has been solved from single-crystal X-ray diffraction data. The compound crystallizes isostructurally with tribromomethyltin(IV), $[SnBr_3(CH_3)]$. The structure consists of compressed tetrahedral molecules that are arranged in infinite chains along the *b* axis. The molecules exhibit point-group symmetry $C_s(m)$ with only a small deviation from the higher $C_{3v}(3m)$ point-group symmetry. The molecules are linked through extremely weak chlorine–tin interactions.

Comment

The structure determination of the title compound was undertaken in order to verify a prediction, derived from