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2-(2-Thioxo-1,3-thiazolidin-3-yl)-4,5-dihydro-1,3-thiazol-1-ium Chloride, $C_6H_9N_2S_3^+.Cl^-$

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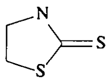
Abstract

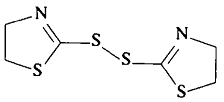
Addition of H_2O_2 to an aqueous solution of 1,3-thiazolidine-2-thione and $CuCl_2.2H_2O$ yielded the title compound. The asymmetric unit consists of one chloride ion and one 2-(2-thioxo-1,3-thiazolidin-3-yl)-4,5-dihydro-1,3-thiazol-1-ium cation, $C_6H_9N_2S_3^+$. The molecular cation consists of 1,3-thiazolidine-2-thione and 4,5-dihydro-1,3-thiazolium moieties in a *cisoid-S,S* configuration, linked by attachment of the thioamido C atom of the thiazolium group to the thioamido N atom of the thiazolidine ring. A combination of ionic and hydrogen-bonded interactions link the molecular cations and the chloride ions in the unit cell.

Comment

The current interest in the coordination chemistry of heterocyclic thioamides (Raper, 1994) is centred on 1,3-thiazolidine-2-thione [tzdtH, (I)] and its anion (tzdt$^-$).



(I)



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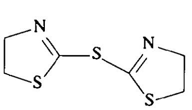

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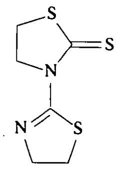
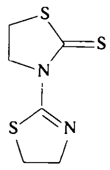


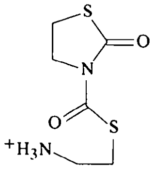
(IV*a*)



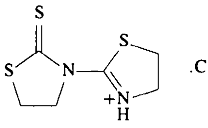
(IV*b*)

The monodentate thione-S ligating behaviour of (I) has been established with a variety of metals including Pd^{II} (Kubiak & Głowiak, 1982), Cd^{II} (Kubiak & Głowiak, 1985) and Zn^{II} (Kubiak & Głowiak, 1987). The anion (tzdt$^-$) can also act as a bridging ligand, displaying both μ_3-(η^2-*S*,η^1-*N*) and μ_4-(η^3-*S*,η^1-*N*) bridging modes in the toluene-solvated polymeric cluster $[\{Cu(tzdt)\}_4(toluene)]_n$ (Raper, Creighton & Clegg, 1995).

The metal-catalyzed oxidation of (I), like that of other organothiones and thiols, is of both chemical and biochemical interest (Sheldon & Rocha, 1981). Its oxidation products, compounds (II)–(IV), may be either isolated or obtained as ligands in the metal complexes which frequently result from metal-catalyzed oxidation (Raper, 1994). Typical of the latter is the *in situ* generation of 2,2′-dithiazolyl disulfide (ttzSSttz), derived from the unsaturated analogue of (I), as an *N,N′*-chelating ligand in $[Fe_2(ttzSSttz)_2Cl_4]$ (Raper, Miller, Głowiak & Kubiak, 1989). The reaction of $ZnCl_2$/tzdtH in concentrated hydrochloric acid, however, produced 2-(2-thioxo-1,3-thiazolidin-3-yl)-4,5-dihydro-1,3-thiazole [tzdtzS, (IV*a*)] in the form of thiazolium cations in $[Zn(tzdtS)Cl_3(H_2O)]$ (Kubiak & Głowiak, 1986). In contrast, the addition of $CuCl_2.2H_2O$ in ethanol to compound (I) in nitromethane yielded compound (IV*b*), seen as an *S,N*-chelating ligand in the halogen-bridged polymer $[CuCl_2(tzdtzS)]_n$ (Ainscough, Anderson, Baker, Bingham, Brader & Brodie, 1985). More vigorous oxidation of an aqueous solution of $ZnCl_2$/tzdtH with H_2O_2 resulted in the production of the (2-oxo-1,3-thiazolidin-3-yl)carbonylthioethylammonium cation (V) (Kubiak, Głowiak & Raper, 1995). Reaction schemes have been proposed to account for the oxidation of heterocyclic thiones (Raper, 1994). They mostly involve the production and subsequent cleavage of the S—S bond in the corresponding heterodisulfides, followed by the production and recombination of thiyl and other free radicals together with the abstraction of oxidized sulfur.



(V)



(VI)

We have extended our study of the oxidation products of thiazole-2-thione derivatives by reacting (I) with $CuCl_2.2H_2O$ and H_2O_2 in aqueous media to produce (IV*a*) as the hydrochloride salt (VI). The asymmetric unit consists of a $C_6H_9N_2S_3^+$ cation and a Cl^- ion (Fig. 1) which are held together by a combination of ionic and hydrogen-bond contacts. The cations essentially consist of 4,5-dihydro-1,3-thiazolium and 1,3-thiazolidine-2-thione rings which are linked through the thioamido C atom of the former to the thioamido N atom of the latter. The location and refinement of a H atom on N21 confirmed the thioamido N atom as the protonation site in the 4,5-dihydro-1,3-thiazolium fragment.

The molecular parameters of the 4,5-dihydro-1,3-thiazolium fragment are similar to those reported for (I) (Raper, Oughtred & Nowell, 1983) and for the

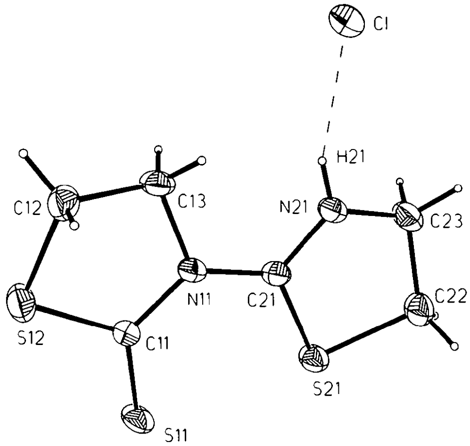


Fig. 1. The molecular structure and numbering scheme of (VI). Displacement ellipsoids are shown at the 50% probability level.

heterocyclic cation in [Zn(tzdtS)Cl$_3$(H$_2$O)] (Kubiak & Głowiak, 1986). In the N-substituted 1,3-thiazolidine-2-thione fragment, however, the thione C—S$_{exo}$ distance [1.643 (4) Å] is shorter and the thioamido C11—N11 distance [1.389 (5) Å] longer than the corresponding mean values reported for (I) (1.676 and 1.315 Å, respectively). These bond-length changes are consistent with an increase in double-bond character of about 15% in the case of the C—S$_{exo}$ bond (Trinajstič, 1968) and a decrease of about 50% in the double-bond character of the endocyclic thioamido C—N distance (Eichorn, 1987). The C21—N11 distance [1.368 (5) Å], which links the two rings, has about 50% double-bond character (Eichorn, 1987). Similar dimensions are reported for the same heterocyclic cation in [Zn(tzdtS)Cl$_3$(H$_2$O)] (Kubiak & Głowiak, 1986). Redistribution of thioamide π-electron density is common among coordinated heterocyclic thionates but invariably involves an increase in the C—N bond length at the expense of the C—S$_{exo}$ bond (Raper, 1994).

The *cisoid-S,S* configuration of the (IV*a*) cation generates a sterically compressed S11···S21 intramolecular contact [2.935 (2) Å] and a dihedral angle of 7.0 (2)° between the C11, C12, C13, S12, N11 and C21, C22, C23, S21, N21 planes. The individual five-membered rings in the heterocyclic cation are similar in conformation. The 1,3-thiazolidine-2-thione ring is twisted about the C12—C13 bond, with these atoms deviating by 0.212 (12) and −0.223 (12) Å from the C11, S12, N11 plane. In the 4,5-dihydro-1,3-thiazolium fragment, the five-membered ring has a twisted conformation, with the C22 and C23 atoms deviating by 0.212 (13) and −0.234 (13) Å from the S21, C21, N21 plane.

The molecular packing is determined by inter-ionic N—H···Cl contacts [N21···Cl 3.068 (4), N21—H21 0.86 (5), H21···Cl 2.24 (5) Å and N21—H21···Cl 161 (4)°].

With H$_2$O$_2$ as the oxidizing agent and in protic media, the heterocyclic cation adopts the *cisoid-S,S* configuration, (IV*a*), in this structure, as it does in [Zn(tzdtS)Cl$_3$(H$_2$O)] (Kubiak & Głowiak, 1986). This form clearly limits the coordinative capacity of the molecule but facilitates intermolecular hydrogen-bonding interactions. In essentially non-protic media, the alternative *S,N*-chelating *transoid-S,S* configuration, (IV*b*), is adopted in polymeric [CuCl$_2$(tzdtzS)]$_n$ (Ainscough *et al.*, 1985).

Experimental

Crystals with well developed faces were obtained by slow evaporation of an aqueous solution. The crystal density D_m was measured by flotation in CCl$_4$/CH$_2$Br$_2$.

Crystal data

$C_6H_9N_2S_3^+.Cl^-$
$M_r = 240.78$
Monoclinic
$P2_1/c$
$a = 11.249\,(2)$ Å
$b = 9.995\,(2)$ Å
$c = 9.362\,(2)$ Å
$\beta = 111.25\,(3)°$
$V = 981.0\,(3)$ Å^3
$Z = 4$
$D_x = 1.630$ Mg m^{-3}
$D_m = 1.61$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9–14°$
$\mu = 0.974$ mm^{-1}
$T = 293\,(2)$ K
Elongated prism
0.35 × 0.30 × 0.30 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2218 measured reflections
1253 independent reflections
1253 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 27.53°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 12$
$l = -12 \rightarrow 10$
2 standard reflections monitored every 50 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0424$
$wR(F^2) = 0.1137$
$S = 1.097$
1253 reflections
146 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0749P)^2 + 0.7261P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.099$

$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.013 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
S11	0.46647 (12)	0.33187 (13)	0.21921 (13)	0.0450 (4)
S12	0.34827 (15)	0.57258 (12)	0.0443 (2)	0.0505 (4)

S21	0.35732 (12)	0.08546 (11)	0.05263 (14)	0.0393 (3)
Cl	−0.02363 (12)	0.25050 (12)	−0.49818 (13)	0.0453 (4)
N11	0.2767 (3)	0.3370 (4)	−0.0614 (4)	0.0313 (8)
N21	0.1732 (4)	0.1489 (4)	−0.1955 (5)	0.0346 (9)
C11	0.3639 (4)	0.4014 (4)	0.0646 (5)	0.032 (1)
C12	0.2349 (6)	0.5664 (5)	−0.1491 (6)	0.044 (1)
C13	0.1796 (5)	0.4269 (5)	−0.1679 (6)	0.040 (1)
C21	0.2617 (4)	0.2013 (4)	−0.0774 (5)	0.0313 (9)
C22	0.2784 (6)	−0.0500 (5)	−0.0804 (7)	0.047 (1)
C23	0.1540 (5)	0.0063 (5)	−0.1871 (7)	0.046 (1)

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

S11—C11	1.643 (4)	N11—C13	1.485 (6)
S12—C11	1.723 (4)	N11—C21	1.368 (5)
S12—C12	1.798 (5)	N21—C21	1.300 (5)
S21—C21	1.741 (4)	N21—C23	1.448 (6)
S21—C22	1.836 (5)	C12—C13	1.511 (7)
N11—C11	1.389 (5)	C22—C23	1.503 (7)
C11—S12—C12	94.8 (2)	S11—C11—S12	121.9 (2)
C21—S21—C22	89.5 (2)	C13—C12—S12	105.1 (3)
C21—N11—C11	125.0 (4)	N11—C13—C12	108.0 (4)
C21—N11—C13	119.7 (3)	N21—C21—N11	121.2 (4)
C11—N11—C13	114.2 (4)	N21—C21—S21	114.6 (3)
C21—N21—C23	115.7 (4)	N11—C21—S21	124.2 (3)
N11—C11—S11	127.3 (3)	C23—C22—S21	106.2 (3)
N11—C11—S12	110.7 (3)	N21—C23—C22	106.4 (4)
C21—N11—C11—S11	0.1 (7)	C23—N21—C21—S21	10.3 (6)
C13—N11—C11—S11	168.1 (4)	C11—N11—C21—N21	176.3 (4)
C21—N11—C11—S12	−177.4 (3)	C13—N11—C21—N21	8.9 (7)
C13—N11—C11—S12	−9.5 (5)	C11—N11—C21—S21	−4.5 (6)
C12—S12—C11—N11	−6.8 (4)	C13—N11—C21—S21	−171.9 (4)
C12—S12—C11—S11	175.5 (3)	C22—S21—C21—N21	6.6 (4)
C11—S12—C12—C13	20.0 (4)	C22—S21—C21—N11	−172.6 (4)
C21—N11—C13—C12	−166.6 (4)	C21—S21—C22—C23	−20.1 (4)
C11—N11—C13—C12	24.8 (6)	C21—N21—C23—C22	−25.7 (6)
S12—C12—C13—N11	−27.3 (6)	S21—C22—C23—N21	28.0 (6)
C23—N21—C21—N11	−170.4 (4)		

The unit-cell parameters and space group were found initially from oscillation and Weissenberg photographs. The structure was solved by direct methods. The H atoms were found from difference synthesis maps and their parameters refined without restriction.

Data collection: *XTL/XTLE* (Syntex, 1976). Cell refinement: *XTL/XTLE*. Data reduction: *XTL/XTLE*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1250). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(7,9-Diphenylcyclopenta[*a*]acenaphthadien-6b-yl)-2-phenylethanol

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Abstract

The synthetic route to obtain single crystals of 2-(7,9-diphenyl-6b*H*-cyclopenta[*a*]acenaphth-6b-yl)-2-phenylethanol, $C_{35}H_{26}O$, is described. There are only weak van der Waals-type forces between neighbouring monomeric molecules.

Comment

We earlier described the use of the cyclopentadienyl derivative 7,9-diphenylcyclopenta[*a*]acenaphthadiene in the preparation of unsymmetric ethylene-bridged zirconocene dichlorides and their use in the polymerization of propene (Rieger, Repo & Jany, 1995*a*,*b*). In this work the ring opening of spiro[(7,9-diphenylcyclopenta[*a*]acenaphthadiene)-8,1′-(2′-phenylcyclopropane)], (2), by reaction with nucleophilic NaCp results in the formation of 1-cyclopentadienyl-2-(7,9-diphenylcyclopenta[*a*]acenaphthadien-8-yl)-1-phenylethane, (4). When KOH was used instead of NaCp to open the cyclopropyl ring, rearrangement of the five-membered ring to give the title compound, (3), took place. The mechanism for this rearrangement is unknown.

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