C(8)	0.6459 (1)	0.9802 (1)	−0.5283 (4)	3.0 (1)
C(8′)	0.6071 (1)	1.0468 (1)	−0.5884 (5)	4.0 (1)
C(9)	0.6283 (1)	0.9327 (1)	−0.3284 (4)	2.8 (1)
C(10)	0.6656 (1)	0.8707 (1)	−0.2714 (4)	2.7 (1)
N(11)	0.7642 (1)	0.7992 (1)	−0.3583 (3)	3.4 (1)
O(12)	0.4087 (1)	0.7903 (1)	0.0940 (4)	5.3 (1)

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

N(1)—C(2)	1.355 (3)	C(5)—C(10)	1.422 (3)
N(1)—C(9)	1.389 (3)	C(5)—N(11)	1.392 (3)
C(2)—O(2)	1.257 (3)	C(6)—C(7)	1.380 (3)
C(2)—C(3)	1.438 (3)	C(7)—C(8)	1.379 (3)
C(3)—C(4)	1.340 (3)	C(8)—C(8′)	1.501 (3)
C(4)—C(10)	1.429 (3)	C(8)—C(9)	1.396 (3)
C(5)—C(6)	1.376 (3)	C(9)—C(10)	1.411 (3)
C(2)—N(1)—C(9)	125.7 (2)	C(6)—C(7)—C(8)	123.1 (2)
N(1)—C(2)—C(3)	115.9 (2)	C(7)—C(8)—C(9)	116.6 (2)
N(1)—C(2)—O(2)	120.8 (2)	C(7)—C(8)—C(8′)	120.9 (2)
O(2)—C(2)—C(3)	123.3 (2)	C(8′)—C(8)—C(9)	122.5 (2)
C(2)—C(3)—C(4)	120.9 (2)	N(1)—C(9)—C(8)	120.6 (2)
C(3)—C(4)—C(10)	121.9 (2)	C(8)—C(9)—C(10)	122.1 (2)
C(10)—C(5)—N(11)	120.7 (2)	N(1)—C(9)—C(10)	117.4 (2)
C(6)—C(5)—N(11)	120.8 (2)	C(5)—C(10)—C(9)	118.8 (2)
C(6)—C(5)—C(10)	118.5 (2)	C(4)—C(10)—C(9)	117.9 (2)
C(5)—C(6)—C(7)	120.8 (2)	C(4)—C(10)—C(5)	123.3 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(12)—H(12*b*)···O(2)	0.99 (6)	1.93 (6)	2.909 (3)	170 (5)
C(8′)—H(8′*b*)···O(2^{i})	0.93 (6)	2.57 (6)	3.228 (3)	128 (5)
N(1)—H(1)···O(2^{i})	0.97 (6)	2.00 (6)	2.966 (3)	175 (5)
O(12)—H(12*a*)···O(12^{ii})	1.10 (7)	1.87 (6)	2.957 (3)	167 (5)
N(11)—H(11*b*)···N(11^{ii})	0.95 (6)	2.25 (6)	3.138 (2)	156 (5)
N(11)—H(11*a*)···O(12^{iii})	0.92 (6)	2.26 (6)	3.177 (3)	170 (5)

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

Data collection, cell refinement and data reduction: *SDP* (Frenz, 1978); structure solution: *SHELXS*86 (Sheldrick, 1985); structure refinement: *SHELX*76 (Sheldrick, 1976); software used to prepare material for publication: *PARST* (Nardelli, 1983), *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1016). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2-Oxo-1,3-thiazolidin-3-yl)carbonylthioethylammonium Nitrate, $C_6H_{11}N_2O_2S_2^+.NO_3^-$

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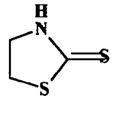
Abstract

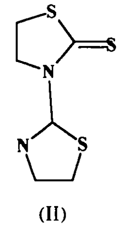
Addition of H_2O_2 to an aqueous solution of 1,3-thiazolidine-2-thione and $ZnCl_2$ produced $ZnSO_4.2H_2O$ and the title compound. The asymmetric unit of the latter consists of one NO_3^- anion and one $C_6H_{11}N_2O_2S_2^+$ cation. The thiazolidine ring has a C(2)-envelope conformation and the exocyclic ketonic and the carbonylic O atoms are *trans* related. The nitrate anions are linked to the cations through hydrogen bonds which involve the H atoms of the ammonium N atoms.

Comment

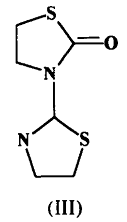
We have reported the syntheses and crystal structures of Pd^{II} (Kubiak & Głowiak, 1982), Cd^{II} (Kubiak & Głowiak, 1985) and Zn^{II} (Kubiak & Głowiak, 1987) complexes of 1,3-thiazolidine-2-thione [tzdtH, (I)], in which the ligand uses its exocyclic thione S atom in monodentate ligation to the metals. In a reaction with $FeCl_2.4H_2O$, the related unsaturated ligand thiazoline-2-thione (tztH) was oxidized to the *N,N*′-chelating 2,2′-dithiazolyl disulfide (ttzSSttz), giving $[Fe_2(ttzSSttz)_2Cl_4]$ (Raper, Miller, Głowiak & Kubiak, 1989). Similarly, the reaction of $ZnCl_2$/tzdtH in concentrated hydrochloric acid also produced an oxidation product, 2-(2-thioxo-1,3-thiazolidin-3-yl)-4,5-dihydro-1,3-thiazole [tzdtzS, (II)], which *S,N*-chelates to the metal in $[Zn(tzdtzS)Cl_3(H_2O)]$ (Kubiak & Głowiak, 1986). Oxidation of (I) by $CuCl_2.2H_2O$ also produced *S,N*-chelating tzdtzS in $[Cu(tzdtzS)Cl_2]_n$; with



(I)



(II)

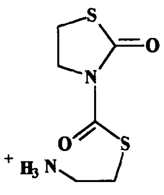


(III)

$Cu(ClO_4)_2.6H_2O$ as the oxidizing agent, oxidative cleavage of (I) produced *S*,*O*-chelating tzdtzO (III), the ketonic analogue of (II), giving $[Cu(tzdtzO)_2(H_2O)_2]$ $(ClO_4)_2$ (Ainscough *et al.*, 1985).

Reaction schemes have been proposed to account for these and other processes which involve the *in situ* oxidation and coordination of heterocyclic thiones (Raper, 1994). They mostly involve the production and subsequent cleavage of the S—S bond in the corresponding hetero-disulfides, followed by the recombination of thiyl and other free radicals with the thione S atom, invariably abstracted as sulfate.

We have extended our study of the oxidation products of thiazole-2-thione derivatives by reacting (I) with $ZnCl_2$ in aqueous solution in the presence of H_2O_2, which produced $ZnSO_4$, subsequently identified in the form of crystalline $ZnSO_4.2H_2O$, in addition to the title compound, (IV).NO_3^-. The presence of SO_4^{2-} and NO_3^- among the reaction products is consistent with the oxidative cleavage of (I). The asymmetric unit of the title compound and the atom-numbering scheme employed are shown in Fig. 1.



(IV)

The title cation, (IV), is the end product of a sequence of oxidation reactions commencing with the replacement of the thioamido H atom in (I) to give the 1,3-thiazolidin-3-yl group, (II), followed by the oxidation of the exocyclic thione of (II) to the corresponding ketone, (III). The sequence is completed by the oxidative cleavage of the 1,3-thiazolidine C(4)—N(2) bond in (III) with production of the C(4)═O(2) bond and protonation of the ammine N(2) atom, to give (IV).

The asymmetric unit of (IV) consists of one $C_6H_{11}N_2O_2S_2^+$ cation and one NO_3^- anion, which are held together by a combination of ionic and hydrogen-bonded contacts. The molecular dimensions of the thiazolidine moiety are very similar to those reported for (I) (Raper, Oughtred & Nowell, 1983) and (II) (Kubiak & Głowiak, 1986), the major difference in both cases being the lengthening of the exocyclic C_{sp^2}—S bond. The C(1)—N(1) distance in (IV) [1.386 (3) Å] is similar to that reported for an N-substituted thiazolidine ring [1.390 (7) Å] (Fujita *et al.*, 1981) and identical to that in (II). The C(1)—O(1) and C(4)—O(2) bond lengths [1.213 (4) and 1.209 (3) Å] are typical of >C═O groups. The formation of the C(4)—O(2) bond in (IV) results in an increase in the C(4)—N(1) and C(4)—S(2) distances [1.380 (3) and 1.773 (2) Å, respectively] relative to the values in (II) [1.341 and 1.740 (6) Å]. Furthermore, cleavage of the thiazolidyl ring at the C(4)—N(2) site alters the geometry of the C(4)—S(2)—C(5)—C(6)—N(2) unit by increasing all the relevant bond angles by 4–8°.

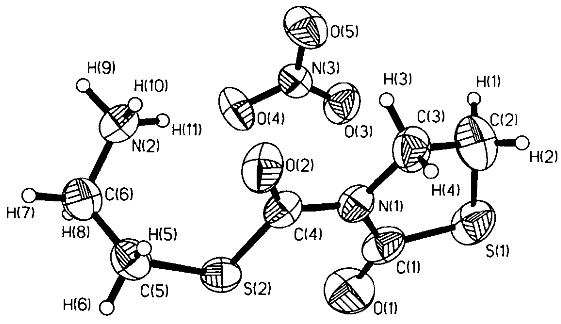


Fig. 1. View of the title compound with atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms are represented by spheres of arbitrary size.

The conformation of (IV) is determined by the van der Waals requirements of the substituents as well as by a combination of ionic and hydrogen bonds. The thiazolidine ring has an envelope conformation with C(2) displaced from the plane of the remaining four atoms by 0.325 (4) Å. O(1) is 0.068 (2) Å out of this plane. The C(1)—N(1)—C(4)—S(2) [−3.3 (3)°] and O(2)—C(4)—S(2)—C(5) [0.7 (3)°] torsion angles indicate that the N(1)—C(4)—S(2)—C(5)—O(2) molecular fragment is essentially planar, with C(6) and N(2) out of this plane by 1.373 (3) and 2.194 (2) Å, respectively. The orientation of the thiazolidinone ring around the N(1)—C(4) bond is such that the exocyclic O(1) atom and the O(2) atom of the carbonyl group are *trans* to each other.

Among the intramolecular distances it is significant that the S(2)···O(1) distance [2.734 (3) Å] is shorter than the sum of the van der Waals radii for these atoms (3.5 Å) (Abrahamsson & Zacharis, 1976). Clearly the electronic interaction between the negatively polarized carbonyl O atom and the positively charged endocyclic S atom is sufficiently strong at this distance to compensate for the repulsive forces between these atoms.

The intramolecular distances between the ammonium N(2) atom and O(2) and C(4) of the carbonyl group are 2.979 (3) and 3.273 (3) Å, respectively. The molecular packing is primarily determined by the NH···O hydrogen bonds formed between the nitrate O atoms and all the H atoms of the ammonium N(2) atoms (Table 2).

The production of the title compound, rather than a Zn^{II} complex of (II), (III) or some other oxidation product of (I), is due to the use of H_2O_2 in the preparation.

Experimental

Clear colourless crystals of the title compound were obtained from the addition of H_2O_2 to a mixture of $ZnCl_2$ and (I) in aqueous solution, followed by slow evaporation of the reaction solution at room temperature (293 K). The crystal density D_m was measured by flotation in CCl_4/CH_2Br_2.

Crystal data

$C_6H_{11}N_2O_2S_2^+.NO_3^-$
$M_r = 269.3$
Monoclinic
$P2_1/c$
$a = 10.567\,(3)$ Å
$b = 11.156\,(3)$ Å
$c = 9.540\,(2)$ Å
$\beta = 95.42\,(4)°$
$V = 1119.6\,(5)$ Å^3
$Z = 4$
$D_x = 1.597$ Mg m^{-3}
$D_m = 1.60$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 8$–$15°$
$\mu = 0.48$ mm^{-1}
$T = 293$ K
Block
$0.45 \times 0.40 \times 0.35$ mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
θ–2θ scans
Absorption correction: none
2615 measured reflections
2580 independent reflections
1961 observed reflections $[F > 7\sigma(F)]$
$R_{\rm int} = 0.053$

$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = -12 \rightarrow 12$
2 standard reflections monitored every 50 reflections
intensity decay: 2%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.041$
$S = 3.81$
1961 reflections
189 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.1$

$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: none
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)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
S(1)	0.3107 (1)	0.7407 (1)	0.3218 (1)	5.6 (1)
S(2)	0.4174 (1)	0.3229 (1)	0.3771 (1)	3.6 (1)
O(1)	0.4432 (2)	0.5481 (2)	0.2703 (2)	6.6 (2)
O(2)	0.2350 (2)	0.3645 (2)	0.5402 (2)	4.6 (1)
O(3)	0.0991 (2)	0.5367 (2)	0.1148 (2)	4.9 (2)
O(4)	0.1228 (2)	0.3480 (2)	0.1582 (2)	4.6 (1)
O(5)	−0.0202 (2)	0.4490 (2)	0.2535 (2)	5.2 (2)
N(1)	0.2858 (2)	0.5264 (2)	0.4191 (2)	3.3 (1)
N(2)	0.1696 (2)	0.1501 (2)	0.3619 (2)	3.8 (2)
N(3)	0.0673 (2)	0.4447 (2)	0.1758 (2)	3.3 (1)
C(1)	0.3577 (3)	0.5905 (2)	0.3307 (3)	4.3 (2)
C(3)	0.1920 (3)	0.5968 (2)	0.4884 (3)	4.5 (2)
C(2)	0.1733 (4)	0.7139 (3)	0.4158 (4)	6.3 (3)
C(4)	0.3007 (2)	0.4072 (2)	0.4557 (2)	3.3 (2)
C(5)	0.3931 (2)	0.1798 (2)	0.4618 (3)	3.8 (2)
C(6)	0.2991 (3)	0.0986 (2)	0.3813 (3)	4.1 (2)

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

C(1)—O(1)	1.213 (4)	C(4)—O(2)	1.209 (3)
C(1)—S(1)	1.748 (3)	C(4)—S(2)	1.773 (2)
C(1)—N(1)	1.386 (3)	S(2)—C(5)	1.818 (3)
S(1)—C(2)	1.803 (4)	C(5)—C(6)	1.501 (4)
C(2)—C(3)	1.483 (4)	C(6)—N(2)	1.480 (4)
N(1)—C(3)	1.470 (3)	N(3)—O(4)	1.246 (3)
N(3)—O(3)	1.242 (3)	N(3)—O(5)	1.240 (3)
N(1)—C(4)	1.380 (3)		
O(1)—C(1)—S(1)	124.9 (2)	C(1)—N(1)—C(4)	126.5 (2)
O(1)—C(1)—N(1)	124.3 (2)	N(1)—C(4)—O(2)	119.2 (2)
S(1)—C(1)—N(1)	110.8 (2)	N(1)—C(4)—S(2)	118.1 (2)
C(1)—S(1)—C(2)	93.2 (1)	C(4)—S(2)—C(5)	98.3 (1)
S(1)—C(2)—C(3)	107.5 (2)	S(2)—C(5)—C(6)	114.6 (2)
C(2)—C(3)—N(1)	109.1 (2)	C(5)—C(6)—N(2)	112.9 (2)
C(3)—N(1)—C(1)	115.5 (2)	O(3)—N(3)—O(5)	119.9 (2)
O(3)—N(3)—O(4)	120.2 (2)	O(4)—N(3)—O(5)	120.1 (2)
C(3)—N(1)—C(4)	117.8 (2)	O(2)—C(4)—S(2)	122.6 (2)
O(1)—C(1)—S(1)—C(2)	172.3 (3)	C(1)—N(1)—C(4)—S(2)	−3.3 (3)
O(1)—C(1)—N(1)—C(4)	1.7 (5)	C(3)—N(1)—C(4)—O(2)	1.5 (3)
C(1)—S(1)—C(2)—C(3)	17.4 (3)	O(2)—C(4)—S(2)—C(5)	0.7 (3)
C(3)—N(1)—C(1)—S(1)	−2.2 (3)	C(4)—S(2)—C(5)—C(6)	91.5 (3)
C(1)—N(1)—C(4)—O(2)	176.1 (4)	S(2)—C(5)—C(6)—N(2)	−62.2 (3)

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

D—H···A	H···A	D···A	D—H···A
N(2)—H(11)···O(4)	1.96 (3)	2.952 (3)	176 (2)
N(2)—H(10)···O(4$^{\rm i}$)	2.05 (3)	2.915 (3)	154 (3)
N(2)—H(9)···O(5$^{\rm ii}$)	1.95 (3)	2.899 (3)	165 (2)

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

Corrections were made for Lorentz and polarization effects. The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Refinement was performed by block-diagonal least squares. H atoms were determined from difference Fourier syntheses. All computations were performed on a NOVA 1200 computer with programs supplied by Syntex *XTL/XTLE* (Syntex, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data, torsion angles and complete geometry have been deposited with the IUCr (Reference: MU1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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