

$S = 1.092$
5744 reflections
475 parameters
H-atom parameters
constrained

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.186 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.188 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Table 1. Selected geometric parameters (Å, °)

C1—O1	1.361 (3)	C1A—O1A	1.349 (3)
C7—N1	1.283 (3)	C7A—N1A	1.298 (3)
C8—O2	1.334 (2)	C8A—O2A	1.341 (2)
C8—N1	1.384 (2)	C8A—N1A	1.374 (2)
C9—C14	1.378 (3)	C9A—C14A	1.370 (3)
C9—O2	1.386 (2)	C9A—O2A	1.391 (2)
C9—C10	1.419 (3)	C9A—C10A	1.430 (3)
C10—O3	1.346 (3)	C10A—C13A	1.349 (3)
C10—C13	1.350 (3)	C10A—O3A	1.349 (2)
C11—C12	1.314 (4)	C11A—C12A	1.313 (4)
C11—O3	1.362 (3)	C11A—O3A	1.389 (3)
C12—C13	1.406 (4)	C12A—C13A	1.451 (4)
C14—C19	1.420 (3)	C14A—C19A	1.434 (3)
C14—C15	1.438 (3)	C14A—C15A	1.445 (3)
C15—C18	1.335 (3)	C15A—O4A	1.343 (3)
C15—O4	1.338 (3)	C15A—C18A	1.343 (3)
C16—C17	1.313 (4)	C16A—C17A	1.317 (4)
C16—O4	1.376 (3)	C16A—O4A	1.383 (3)
C17—C18	1.458 (3)	C17A—C18A	1.463 (3)
O1—C1—C6	122.1 (2)	O1A—C1A—C6A	121.6 (2)
O1—C1—C2	115.9 (2)	O1A—C1A—C2A	114.9 (2)
O2—C8—N1	122.2 (2)	O2A—C8A—N1A	121.3 (2)
C19—C8—N1	127.8 (2)	C19A—C8A—N1A	128.5 (2)
C14—C9—C10	136.7 (2)	C14A—C9A—C10A	135.8 (2)
O2—C9—C10	114.3 (2)	O2A—C9A—C10A	114.9 (2)
O3—C10—C9	117.3 (2)	C13A—C10A—C9A	134.1 (2)
C13—C10—C9	133.1 (2)	O3A—C10A—C9A	115.5 (2)
C9—C14—C15	131.3 (2)	C9A—C14A—C15A	130.5 (2)
C19—C14—C15	123.5 (2)	C19A—C14A—C15A	123.9 (2)
C18—C15—C14	129.9 (2)	O4A—C15A—C14A	120.8 (2)
O4—C15—C14	121.1 (2)	C18A—C15A—C14A	129.1 (2)
C8—C19—C20	122.6 (2)	C8A—C19A—C20A	123.7 (2)
C14—C19—C20	129.2 (2)	C20A—C19A—C14A	128.8 (2)
N2—C20—C19	177.6 (2)	N2A—C20A—C19A	175.9 (2)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...N1	0.82 (4)	1.88 (4)	2.596 (2)	147 (4)
O1A—H1A...N1A	0.81 (4)	1.91 (3)	2.605 (3)	142 (4)
C3A—H3A...N2 ⁱ	0.96	2.53	3.385 (4)	149
C12—H12...N2 ⁱⁱ	0.96	2.41	3.341 (4)	163
C13—H13...O4	0.96	2.26	2.962 (3)	130
C13A—H13A...O4A	0.96	2.39	2.993 (3)	121
C4—H4...O3A	0.96	2.83	3.406 (4)	120
C16A—H16A...O3	0.96	2.74	3.337 (4)	121
C17A—H17A...O3	0.96	2.88	3.399 (4)	115
C16—H16...N2A ⁱⁱⁱ	0.96	2.68	3.354 (4)	128

Symmetry codes: (i) $x-1, 1+y, z-1$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, 1-z$.

The structure was solved by direct-phase determination. The parameters of the complete structure could be refined by full-matrix least-squares methods including anisotropic displacement parameters for non-H atoms. H atoms bonded to C atoms were refined using a riding model and H-atom displacement parameters were restricted to be $1.2U_{\text{eq}}$ of the parent atom. The hydroxyl H atoms were located in a difference electron-density map and their positions were allowed to refine, but their displacement parameters were also constrained to be $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *Nonius Diffractometer Control Software* (Nonius GmbH, 1993). Cell refinement: *Nonius Diffractometer Control Software*. Data reduction: *REDU4* (Stoe & Cie, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1070). Services for accessing these data are described at the back of the journal.

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Ethyl mustard oil sulfide hydrochloride

JOHANNES BECK AND JÖRG WALTER

Institut für Anorganische und Analytische Chemie I, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany. E-mail: johannes.beck@anorg.chemie.uni-giessen.de

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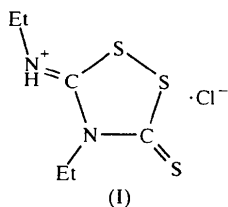
Abstract

In the title compound, *N*-(4-ethyl-5-thioxo-1,2,4-dithiazolidin-3-ylidene)ethylammonium chloride, C₆H₁₁N₂S₃·Cl[−], the five-membered C₂NS₂ ring is essentially

planar. The bond lengths indicate that the molecule is stabilized through some π -orbital delocalization. This delocalization is less pronounced in the disulfide function, where the S—S bond length is 2.069 (1) Å.

Comment

Pseudohalides of transition metals in high oxidation states can be synthesized by reaction of transition metal halides, oxide halides and sulfide halides with pseudohalide anions (Funk & Böhlend, 1963; Sharma & Rastogi, 1981; Musleh *et al.*, 1986). We used ethylisothiocyanate as the pseudohalide source; its reaction with WOCl_4 yielded crystals of the title compound which consists formally of two molecules of ethylisothiocyanate joined together with an additional S atom to form a five-membered ring, and one molecule of HCl. The free base belongs to a group of five-membered heterocyclic compounds called mustard oil sulfides and conforming to the chemical formula $(R\text{—NCS})_2\text{S}$. These have been known for a long time (Freund, 1895), but only a few of them have been characterized by X-ray analysis (Stanford, 1963; Hordvik, 1963; Raston *et al.*, 1974; Fahrenholtz *et al.*, 1980). The title structure, (I), is the first example of a mustard oil sulfide in the imine form (Tittelbach, 1991) with only aliphatic substituents.



The ring is approximately planar with the ring atoms having a maximum displacement of 0.025 (1) Å from their least-squares plane. The planarity of the ring, together with the observed bond lengths, suggests that there is some π -orbital delocalization in the molecule. This delocalization seems to be less pronounced in the disulfide part; while all other intra-ring distances are appreciably shorter than normal single bonds, the S1—S2 distance of 2.069 (1) Å is even longer than the observed values [2.052 (4) (Stanford, 1963) and 2.063 (5) Å (Hordvik, 1963)] for a not-significantly shortened S—S single bond in xanthan hydride, the N-unsubstituted 5-imino-1,2,4-dithiazolidine-3-thione. The exocyclic C1—N1 bond length is 1.292 (3) Å, significantly shorter than the intra-ring C—N bond lengths [1.366 (3) and 1.382 (3) Å]. This, together with the deviation of N1 from the least-squares plane through the five-membered ring [0.058 (3) Å] and comparison with the nearly equal C—N bond lengths in xanthan hydride, suggests that the exocyclic C—N bond in the title compound contributes weakly to delocalization, and indi-

cates the imine form. The exocyclic C2—S3 bond is also shorter [1.624 (3) Å] than in xanthan hydride [1.650 (9) (Stanford, 1963) and 1.653 (9) Å (Hordvik, 1963)] and the distance of S3 from the ring plane [0.118 (3) Å] also results in a smaller contribution to delocalization.

Hydrolysis of WOCl_4 by traces of water is a source of HCl and causes the formation of a hydrochloride with the H atom located at the exocyclic N atom. The shortest Cl...H distance of 2.35 (3) Å represents only a weak hydrogen bond.

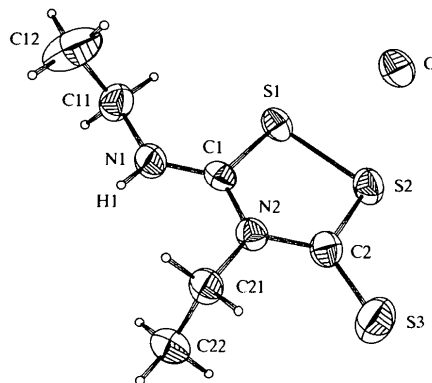


Fig. 1. An ORTEP (Johnson, 1976) drawing of the asymmetric unit in the structure of *N*-(4-ethyl-5-thioxo-1,2,4-dithiazolidin-3-ylidene) ethylammonium chloride. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn with an arbitrarily reduced radius.

Experimental

$\text{C}_6\text{H}_{11}\text{ClN}_2\text{S}_3$ can be prepared by oxidation of ammonium *N*-alkyldithiocarbamates with bromine (Freund & Bachrach, 1895). In this work it was obtained as a by-product by reaction of WOCl_4 with $\text{C}_2\text{H}_5\text{NCS}$ as solvent under an argon atmosphere at 346 K for 4 h, followed by vacuum evaporation of the solvent. After some weeks, the viscous residue partly crystallized and ethyl ammonium chloride was identified by X-ray analysis. After treatment of the residue with tetrahydrofuran and vacuum evaporation at 343 K, a few crystals of the title compound sublimed out of the residue.

Crystal data

$\text{C}_6\text{H}_{11}\text{N}_2\text{S}_3 \cdot \text{Cl}^-$
 $M_r = 242.82$
 Monoclinic
 $P2_1/c$
 $a = 9.327 (5) \text{ \AA}$
 $b = 17.472 (8) \text{ \AA}$
 $c = 7.296 (4) \text{ \AA}$
 $\beta = 115.51 (4)^\circ$
 $V = 1073.1 (10) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.503 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 236 reflections
 $\theta = 4.82\text{--}25.49^\circ$
 $\mu = 0.890 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Rectangular plate
 $0.53 \times 0.38 \times 0.08 \text{ mm}$
 Translucent pale yellow

Data collection

Stoe Imaging Plate	6577 measured reflections
Diffraction System (IPDS) diffractometer	1959 independent reflections
IPDS scans	1726 reflections with $I > 2\sigma(I)$
Absorption correction:	$R_{\text{int}} = 0.043$
Gaussian (HABITUS; Herrendorf, 1993)	$\theta_{\text{max}} = 25.95^\circ$
$T_{\text{min}} = 0.715$, $T_{\text{max}} = 0.931$	$h = -11 \rightarrow 11$
	$k = -21 \rightarrow 21$
	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.6557P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.063$	$\Delta\rho_{\text{max}} = 0.352 \text{ e } \text{Å}^{-3}$
1959 reflections	$\Delta\rho_{\text{min}} = -0.406 \text{ e } \text{Å}^{-3}$
113 parameters	Extinction correction: none
H atoms treated by a mixture of independent and constrained refinement	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—C1	1.747 (2)	C11—C12	1.480 (5)
S1—S2	2.069 (1)	C1—N2	1.366 (3)
S2—C2	1.735 (3)	N2—C2	1.382 (3)
S3—C2	1.624 (3)	N2—C21	1.486 (3)
N1—C1	1.292 (3)	C21—C22	1.505 (4)
N1—C11	1.466 (3)		
C1—S1—S2	93.55 (9)	C1—N2—C2	118.7 (2)
C2—S2—S1	96.17 (9)	N2—C2—S2	114.6 (2)
N2—C1—S1	116.8 (2)		

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...Cl ¹	0.81 (3)	2.35 (3)	3.140 (3)	166 (3)

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

Atom positions were obtained by direct methods as well as from Patterson maps. All non-H atoms were refined anisotropically. The H atom attached to the N atom was located from a $\Delta\rho$ map and refined isotropically. All other H atoms were treated as riding atoms.

Data collection: *IPDS* (Stoe & Cie, 1995). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1288). Services for accessing these data are described at the back of the journal.

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1,2:5,6-Di-O-isopropylidene- α -D-glucopyranosyl (S)-cyclohexanesulfinate

CAROLE ALAYRAC,^a JEAN-FRANÇOIS SAINT-CLAIR,^a MARGARETH LEMARIÉ,^a PATRICK METZNER^a AND MARIE-THÉRÈSE AVERBUCH-POUCHOT^b

^aLaboratoire de Chimie Moléculaire et Thio-organique, UMR CNRS 6507, ISMRA-Université, 6 Boulevard du Maréchal Juin, 14050 Caen, France, and ^bLEDSS, UMR CNRS 5616, Université Joseph Fourier, BP53, 38041 Grenoble CEDEX 9, France. E-mail: marie-therese.averbuch@ujf-grenoble.fr

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Abstract

The first crystal structure of a chiral diacetone-D-glucose (DAG) sulfinate, C₁₈H₃₀O₇S, is reported. The absolute configuration (S) of the S atom is assigned. Previous assignments of the stereochemistry of analogous DAG sulfonates were only made indirectly by their transformation into known sulfoxides *via* an S_N2 process.

Comment

Sulfoxides are very useful tools as chiral inductors in asymmetric synthesis. One of the major methods of obtaining such molecules involves the reaction of a chiral sulfinate with a Grignard reagent. This transformation, called the Andersen synthesis (Andersen, 1962, 1964), proceeds with inversion of configuration at sulfur. It