X-Ray Structural Analysis and Vibrational Spectra of Sodium Cysteine-S-sulfonate, ${}^+\text{H}_3\text{NCH}(\text{COO}^-)\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 3/2\text{H}_2\text{O}$ [1]

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Dedicated to Prof. Dr. Dr. Techn. h.c. Ulrich Wannagat on the occasion of his 70th birthday

Z. Naturforsch. **48b**, 555–560 (1993); received July 23, 1992

Cysteine, S-Sulfonate, Structure, Spectra, Hydrogen Bonds

The title compound crystallizes orthorhombically (space group C 222₁) with $a = 797.0$, $b = 870.3$ and $c = 2739.0$ pm. The anions are zwitterions which are heavily involved in intra- and intermolecular $\text{NH} \cdots \text{O}$ and $\text{OH} \cdots \text{O}$ hydrogen bonding. The two types of sodium cations are coordinated by six oxygen atoms each of which belongs to either SO_3 groups (Na2) or water molecules and SO_3 groups (Na1). A second type of water molecules is not coordinated to the cations. The SS bond length is 208.2 pm. Infrared and Raman spectra of the title compound are reported and tentatively assigned. The SS stretching vibration is observed at 409 cm^{-1} .

Introduction

Cystine is an important constituent of most proteins. Its disulfide bond links parts of the amino acid chains and is therefore responsible for the three-dimensional structure of the protein. Reductive or nucleophilic cleavage of the disulfide bridges change the chemical and physical properties of the proteins considerably. The two most important nucleophiles in this context are sulfide (S^{2-} and HS^-) and sulfite (SO_3^{2-}) which react with organic disulfides according to eq. (1) and (2) [2–9]:

In the case of cysteine (bis-alanyl-disulfane) the “persulfide” (RSS^-) (alanyldisulfide) has been found to undergo autoxidation in air; eq. (3) [10]:

The cysteine-S-sulfonate **1** is also formed on treatment of cysteine with thiosulfate at $\text{pH} \approx 7$ [11]:

Small amounts of **1** are formed on UV irradiation of aqueous cysteine in the presence of air

[12]. However, the most convenient preparation of **1** starts from cysteine and sodium tetrathionate and results in pure crystals of composition $\text{C}_3\text{H}_6\text{O}_5\text{NS}_2\text{Na} \cdot 3/2\text{H}_2\text{O}$ [13]:

In this work we report the Raman and infrared spectra as well as the crystal and molecular structure of $\text{H}_3\text{N}^+\text{CH}(\text{COO}^-)\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 3/2\text{H}_2\text{O}$.

X-Ray Structural Analysis

A single crystal of **1** of dimensions $0.5 \times 0.3 \times 0.3\text{ mm}^3$ was grown from aqueous ethanol (70/30 v/v $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$) by cooling to 4°C . Using an automated CAD4 diffractometer (2θ - ω scan) 1880 reflections were measured at 22°C ($0 \leq 2\theta \leq 55^\circ$) of which 838 were classified as observed [$I \geq 2\sigma(I)$]. A summary of crystallographic data is given in Tab. I.

The structure was solved by direct methods (program SHELXS-86 [14]) and refined using the program SHELXS-76 [15]. Lorentz and polarization corrections were applied. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of the anion of **1** could be localized refined isotropically. The refinement resulted in $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o| = 0.04$. The fractional coordinates, bond lengths, bond angles, and torsional angles are given in Tables II–V and the

* Reprint requests to Prof. Dr. R. Steudel.

Compound	$\text{H}_3\text{NCH}(\text{COO})\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 1.5\text{H}_2\text{O}$
Formula	$\text{C}_3\text{H}_6\text{NS}_2\text{O}_5\text{Na} \cdot 1.5\text{H}_2\text{O}$
Formula weight	250.2
Space group	$\text{C}22_1$
Systemat. absences	$h0l (h = 2n+1), 00l (l = 2n+1), h+k = 2n+1, k = 2n+1$
a [pm]	797.0(1)
b [pm]	870.3(8)
c [pm]	2739.0(1)
V [nm ³]	1.899
Density [gcm ⁻³], calculated	1.624
Molecules in unit cell (Z)	8
$F(000)$, electrons	952
Radiation	$\text{MoK}\alpha$ (graphite-monochromated), $\lambda = 71.07$ pm
lin. absorpt. coeff. μ ($\text{MoK}\alpha$) [cm ⁻¹]	5.7

Table I. Summary of crystallographic data (standard deviations in brackets).

Table II. Fractional atomic coordinates for $\text{H}_3\text{NCH}(\text{COO})\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 1.5\text{H}_2\text{O}$. For numbering of atoms see Fig. 2.

Atom	x/a	y/b	z/c
S(1)	0.1411(2)	0.2131(2)	0.3123(1)
S(2)	0.1888(3)	0.1766(2)	0.3861(1)
O(1)	0.2466(7)	0.3375(6)	0.2963(2)
O(2)	0.1851(8)	0.0656(6)	0.2918(2)
O(3)	-0.0344(7)	0.2549(8)	0.3078(2)
O(4)	0.2900(8)	0.6875(6)	0.4677(2)
O(5)	0.1211(8)	0.7001(7)	0.4037(2)
N	0.4196(8)	0.4159(8)	0.4426(2)
C(1)	0.1364(10)	0.3656(9)	0.4102(3)
C(2)	0.2854(10)	0.4772(8)	0.4107(3)
C(3)	0.2270(10)	0.6345(8)	0.4296(2)
Na(1)	0.5000(0)	0.3879(4)	0.2500(0)
Na(2)	0.0000(0)	0.4943(6)	0.7500(0)
H(1)	0.4700(8)	0.4800(8)	0.4490(2)
H(2)	0.4770(12)	0.3540(11)	0.4310(3)
H(3)	0.3360(13)	0.4900(11)	0.3670(3)
H(4)	0.6410(17)	0.3690(13)	0.0130(4)
H(5)	0.0880(8)	0.3400(7)	0.4440(2)
H(6)	0.0469(13)	0.4180(10)	0.3900(3)
O(6)	0.7064(0)	0.5000(0)	0.5000(0)
H(7)	0.7510(14)	0.4430(11)	0.4810(3)
H(8)	0.7510(14)	0.5570(11)	0.5190(3)
O(7)	0.6112(6)	0.1877(6)	0.3017(2)

Table III. Interatomic distances [pm] in $\text{H}_3\text{NCH}(\text{COO})\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 1.5\text{H}_2\text{O}$ (standard deviations in brackets).

Bonds	Distances	Bonds	Distances
S(1)–S(2)	208.2(4)	S(1)–O(1)	143.9(6)
S(1)–O(2)	144.5(6)	S(1)–O(3)	145.1(6)
S(2)–C(1)	181.9(8)	C(1)–C(2)	153.4(11)
C(2)–C(3)	153.6(10)	N–C(2)	148.0(10)
O(4)–C(3)	124.7(8)	O(5)–C(3)	124.2(9)
C(1)–H(5)	103(6)	C(1)–H(6)	101(9)
C(2)–H(3)	127(9)	N–H(1)	71(7)
N–H(2)	78(9)	N–H(4)	137(11)
Na(1)–O(1)	242.5(6)		

S(2)–S(1)–O(1)	107.7(3)	S(2)–S(1)–O(2)	101.4(3)
S(2)–S(1)–O(3)	107.3(3)	O(1)–S(1)–O(2)	114.1(3)
O(1)–S(1)–O(3)	110.4(4)	O(2)–S(1)–O(3)	115.1(4)
S(1)–O(1)–Na(1)	141.5(3)	S(1)–S(2)–C(1)	99.8(3)
S(2)–C(1)–C(2)	113.5(5)	C(1)–C(2)–C(3)	109.5(6)
C(2)–C(3)–O(4)	119.3(7)	C(2)–C(3)–O(5)	115.0(6)
O(4)–C(3)–O(5)	125.6(7)	C(1)–C(2)–N	109.7(6)
N–C(2)–C(3)	109.9(6)	C(2)–N–H(1)	106.0(50)
C(2)–N–H(2)	116.0(60)	C(2)–N–H(4)	111.0
H(1)–N–H(2)	108.0(90)	H(1)–N–H(4)	102.0
H(2)–N–H(4)	110.0	S(2)–C(1)–H(5)	102.0(30)
S(2)–C(1)–H(6)	112.0(50)	C(2)–C(1)–H(5)	115.0(30)
C(2)–C(1)–H(6)	106.0(50)	N–C(2)–H(3)	111.0(50)
H(5)–C(1)–H(6)	109.0(60)	C(3)–C(2)–H(3)	110.0(40)
C(1)–C(2)–H(3)	107.0(40)		

Table IV. Selected bond angles [deg] of $\text{H}_3\text{NCH}(\text{COO})\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 1.5\text{H}_2\text{O}$.

O(1)–S(1)–S(2)–C(1)	58.7(4)	O(3)–S(1)–S(2)–C(1)	– 60.2(4)
O(2)–S(1)–S(2)–C(1)	178.8(4)	S(2)–S(1)–O(1)–Na(1)	104.2(5)
O(2)–S(1)–O(1)–Na(1)	– 7.6(6)	O(3)–S(1)–O(1)–Na(1)	– 138.9(5)
C(2)–C(1)–S(2)–S(1)	– 89.2(6)	S(2)–C(1)–C(2)–N	– 61.4(7)
S(2)–C(1)–C(2)–C(3)	177.9(5)	C(1)–C(2)–C(3)–O(4)	118.5(8)
C(1)–C(2)–C(3)–O(5)	– 63.4(8)	N–C(2)–C(3)–O(4)	– 2.1(9)
N–C(2)–C(3)–O(5)	176.0(6)		

Table V. Selected dihedral angles [deg] of $\text{H}_3\text{NCH}(\text{COO})\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 1.5\text{H}_2\text{O}$.

crystal and molecular structure is shown in Fig. 1 and 2*.

The sodium cations are located on special positions; there are two half cations per anion which

Fig. 1. Unit cell of $\text{H}_3\text{NCH}(\text{COO})\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 1.5\text{H}_2\text{O}$. Blank circles are oxygen atom of water molecules, crossed circles are sodium cations.

Fig. 2. Molecular structure of the L-cysteine-S-sulfonate anion and numbering of atoms.

* Further details of the crystal structure analysis may be requested from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, citing the deposition number CSD 56521, the authors and the journal source.

have different coordination spheres as will be discussed below.

The anion of **1** is a zwitterion of C_1 symmetry with the amino group protonated and the carboxyl group deprotonated (see Fig. 2). The same situation has been observed for L-cysteine [16, 17]. The chain-like anion is of helical structure: the torsional angles S–S–C–C and S–C–C–N amount to -89° and -61° , respectively. The carboxyl group is practically coplanar with the neighboring CN unit (dihedral angles $\text{N–C2–C3–O4} = 2.1^\circ$ and $\text{N–C2–C3–O5} = 176.0^\circ$). The positions of the hydrogen atoms of **1** could only approximately be determined and therefore the CH, NH and OH bond distances are found in the large range of 70–137 pm. Nevertheless, quite a number of intra- and intermolecular hydrogen bonds could be identified which certainly will contribute to the overall conformation of the anion. The strongest intramolecular hydrogen bond connects the NH_3^+ and COO^- groups. The distance $\text{H1} \cdots \text{O4}$ is only 236 pm (van der Waals distance 270 pm) while the distance $\text{H4} \cdots \text{O4}$ is 288 pm. The $\text{H1} \cdots \text{O4}$ interaction may be responsible for the almost coplanar arrangement of atoms N, C2, C3, O4 which minimizes the N–O4 distance. There are also relatively close contacts between the oxygen atoms of the sulfonate group and some of the hydrogen atoms linked to C2 and C1 (e.g., $\text{H3} \cdots \text{O1} = 247$ pm).

Most important are the hydrogen bonds between neighboring anions and between the structural water molecules (H7–O6–H8) and the anions. Fig. 1 shows that neighboring anions are linked both by cations and by $\text{C3–O4} \cdots \text{H4–N}$ bridges. The intermolecular $\text{H4} \cdots \text{O4}$ distance is only 144 pm and the N–H4–O4 angle amounts to 177° . The distance $\text{N} \cdots \text{O4}$ is 267 pm, a value very similar to the values observed in amino acids and small peptides. There are two such interactions between each pair of neighboring anions. Although the positions of H atoms cannot be determined very accurately by X-ray diffraction, the

geometrical parameters just mentioned together with the bond distance N–H4 of 137 pm show that strong N–H–O bridges are present.

The second carboxylic oxygen atom (O5) is also involved in intermolecular hydrogen bonding since the distance N–H2···O5 amounts to 192 pm. With other words, each NH₃ group is triply hydrogen bridged: *via* H1 to the intramolecular O4, *via* H2 to an intermolecular O5 and *via* H4 to O4 of a neighboring molecule. The strength of these bridge bonds increases in that order. Since H4 is 137 pm apart from its nitrogen neighbor but 144 pm from its oxygen bridge head, a small shift of H4 towards the oxygen atom would transform the zwitterion into a normal monoanion with –NH₂ and –COOH groups. A similar three-dimensional intermolecular network of hydrogen bonds has been observed for L-cysteine [17].

The structural water molecules H7–O6–H8 are located on special positions (mirror planes) and are hydrogen bonded to four different anions as shown in Fig. 3. The distances N–H1···O6 of 235 pm and O6–H7···O4 of 228 pm indicate relatively weak hydrogen bonds; the coordination of O6 is a distorted tetrahedron. There is one such H₂O molecule per two anions.

Despite the low degree of symmetry in the anion the carboxyl group shows two equal C–O distances of 124.5 pm; the O–C–O angle amounts to 125.6°. The bond angles at the nitrogen atom are in the range of 106–116°. The thiosulfate group exhibits the expected distorted tetrahedral structure with an average S–O bond length of 144.5 pm and an S–S distance of 208.2 pm. For comparison, the S–S bond length of 2-aminoethane-thiosulfuric acid, ⁺H₃N–C₂H₄–S₂O₃[–] [18], has

Fig. 3. Pseudo-tetrahedral coordination of the structural water molecules which are located on mirror planes.

been determined as 205.4 pm. This zwitterionic compound is also heavily involved in intra- and intermolecular hydrogen bonding. In the case of L-cysteine the S–S bond length is 203.2 pm (hexagonal form) [19] and 204.3 pm (tetragonal form) [20], respectively. The CC, CS, CN and CO bond length are all very close to the values reported for L-cysteine [17].

The sulfonate groups of neighboring anions of **1** are bridged by sodium cations (see Fig. 1). There are two types of cations: type 1 (Na2) is coordinated by six oxygen atoms belonging to four different anions, and type 2 (Na1) is coordinated by two water molecules and four oxygen atoms (O1 or O2) of four different anions. The hydrogen atoms of these two water molecules could not be located. The distances Na2–O are in the range 270–280 pm and the angles O–Na2–O are ranging from 51–159°. This coordination, although of C_s symmetry, is far from being octahedral. The same holds for the coordination sphere of Na1. The distances Na1–O are in the narrow range of 141–142 pm. A second type of water molecules is located on a special position (H7–O6–H8) and not coordinated to any cation. Since only one such H₂O molecule is present per 2 formula units, the overall water content is 1.5 H₂O per formula.

Vibrational Spectra

In Table VI the results of the infrared and Raman spectroscopic investigation of solid **1** are listed. The IR and Raman spectra are both highly characteristic and may be used to identify the compound. The vibrational assignment given in Table VI is tentative and based on the accurate assignments of the spectra of L-cysteine [21] and various ionic thiosulfates [22, 23], polythionates [24] as well as the hydrogenthiosulfate ion HS₂O₃[–] [23]. The most intense Raman line at 409 cm^{–1} is assigned to the SS stretching vibration which has been observed at 403 cm^{–1} in HS₂O₃[–] [23] and near 390 cm^{–1} in polythionates [24]. Of very high Raman and infrared intensity is the symmetrical stretching mode of the SO₃ group near 1045 cm^{–1}, whereas the asymmetrical SO₃ stretch at 1218 cm^{–1} gives rise to a strong IR but weak Raman band.

With 48 vibrational degrees of freedom of the anion and 8 molecules in the unit cell the spectrum of **1** is too complex for any detailed analysis unless

Table VI. Raman and infrared spectra of solid $\text{H}_3\text{NCH}(\text{COO})\text{CH}_2\text{S}_2\text{O}_3\text{Na} \cdot 1.5\text{H}_2\text{O}$ at 20 °C (wave-numbers in cm^{-1} ; Raman intensities in brackets; abbrev.: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, ν = stretching, δ = bending, ρ = rocking, γ = wagging, τ = torsion).

Raman	Infrared	Assignment
53 (46)		
64 (39)		
88 (29)		
111 (37)		δCCS
140 (sh)		
153 (25)		
188 (sh)		
205 (34)		τCOO^-
219 (34)		δSSO
235 (14)		δSSC
309 (29)		
328 (1)	322 w	$\delta_s\text{SO}_3$
363 (31)	362 m	
409 (100)	408 vw	νSS
428 (sh)	426 w	
473 (16)	460 w, b	τNH_3
535 (8)	532 vw	$\delta_{\text{as}}\text{SO}_3$
550 (8)	554 sh	
565 (8)	566 m	δCCO
651 (sh)	636 s	δCOO^-
660 (19)		νCS
687 (10)	686 vw	
807 (7)	808 w	
832 (13)	832 w	γCOO^-
924 (10)	922 w	ρNH_3
943 (7)	942 m	
1049 (40)	1038 vs	$\nu_s\text{SO}_3$
1075 (6)	1075 vw	
1102 (6)	1102 w	ρNH_3
1134 (6)	1132 w	
	1136 sh	
1214 (6)	1218 vs	$\nu_{\text{as}}\text{SO}_3 + \gamma\text{CH}_2$
1245 (9)	1236 s	
1308 (6)	1306 w	
	1352 w	
1350 (12)	1360 m-s	δCH
1400 (9)	1400 s	δCH_2
1416 (8)	1415 w	
	1528 s	$\delta_s\text{NH}_3$
	1570 w	$\delta_{\text{as}}\text{NH}_3$
	1610 sh	$\delta\text{H}_2\text{O}$
	1632 vs	$\nu_{\text{as}}\text{COO}^-$
	2030 w, b	$\nu\text{N-H4}$
	2420 vw, b	combination and overtones
	2500 vw, b	
	2620 vw, b	
	2760 vw, b	
2812 (8, b)		
2920 (29)	2925 vw	$\nu\text{CH and CH}_2$
2964 (10)	2960 w, b	
2979 (10)	2980 w, b	$\nu\text{N-H2}$
3222 (6, b)	3220 m	$\nu\text{N-H1}$
3440 (6, b)	3440 w	$\nu_s\text{H}_2\text{O}$
3537 (5, b)	3540 m	$\nu_{\text{as}}\text{H}_2\text{O}$

isotopic substitution is carried out. Therefore, a simple deuteration experiment was carried out by recrystallization of **1** from D_2O which exchanges the labile H atoms linked to either oxygen or nitrogen for D. The infrared spectrum of the deuterated product showed that the following absorptions of **1** had shifted to lower wavenumbers: 3540, 3440, 3220, 2980, 2030, 1610, 1570, 1528, 1132, 1102, 942, 922, and 460 cm^{-1} . Therefore, these bands have been assigned as shown in Table VI. Some of the bending and rocking modes of the $-\text{NH}_3$ group occur as two neighboring bands of unequal intensity.

Discussion

This work confirms the chemical composition of **1** which originally was given with 1.5 H_2O per formula unit [5] while later authors used a formula with 2 H_2O per sodium atom [13]. Surprisingly, there are two types of H_2O molecules and two types of sodium cations but only one type of anions in the structure of **1**, which is three-dimensionally linked by a network of $\text{NH}\cdots\text{O}$ and $\text{OH}\cdots\text{O}$ hydrogen bonds. These bridging bonds not only show up in the close contacts of the corresponding atoms but also in the vibrational spectra: the NH stretching vibrations of the $-\text{NH}_3^+$ group are partly observed at lower wavenumbers ($3220\text{--}2812\text{ cm}^{-1}$) than the corresponding vibrations of L-cysteine ($3166\text{--}3064\text{ cm}^{-1}$ [14]). In addition to the intermolecular hydrogen bonds there are also strong intraanionic $\text{NH}\cdots\text{O}$ interactions. This complex network of hydrogen bonds is probably responsible for the torsional angles at the various comparable CC axes which are very different in **1**, in orthorhombic L-cysteine [17] and in the two independent molecules of monoclinic L-cysteine [16]. For example, the torsional angle S-C-C-C amounts to 178° in **1**, -17° in orthorhombic L-cysteine, and -51° and 68° in monoclinic L-cysteine. Similarly, the angles S-C-C-N vary between -170° and 73° .

Experimental

1 was prepared as colorless crystals according to ref. [13].

Analytical data:

Calcd	C 14.4	H 3.6	N 5.6	S 25.6%,
Found	C 14.2	H 3.7	N 5.4	S 25.5%.

The spectroscopic equipment used has been described earlier [24, 25]. IR spectra were recorded of KBr discs.

Financial support by the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie is gratefully acknowledged.

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