Redetermination of bis(S-methyl-thiuronium) sulfate

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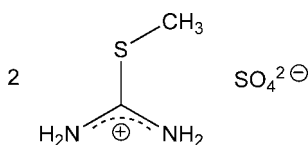Correspondence e-mail: axel.schulz@uni-rostock.de

The single-crystal structure determination of the title compound, $2C_2H_7N_2S^+ \cdot SO_4^{2-}$, confirms the previous structure determination [Stam (1962). *Acta Cryst.* **15**, 317–322]. The present study includes the determination of the H-atom parameters, which revealed several interionic N—H···O hydrogen bonds. The S atom of the sulfate anion is situated on a crystallographic twofold rotation axis.

Related literature

For an alternative method of preparation, see: Arndt (1921).

Experimental

Crystal data

$2C_2H_7N_2S^+ \cdot SO_4^{2-}$	$V = 1197.6\ (4)$ Å^3
$M_r = 278.37$	$Z = 4$
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
$a = 11.3250\ (19)$ Å	$\mu = 0.62$ mm^{-1}
$b = 8.3903\ (18)$ Å	$T = 295\ (2)$ K
$c = 12.6041\ (17)$ Å	$0.57 \times 0.53 \times 0.47$ mm

Data collection

Nonius MACH3 diffractometer	1175 measured reflections
Absorption correction: ψ scan	1173 independent reflections
(North *et al.*, 1968)	1098 reflections with $I > 2\sigma(I)$
$T_{min} = 0.717$, $T_{max} = 0.749$	$R_{int} = 0.006$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of
$wR(F^2) = 0.092$	independent and constrained
$S = 1.08$	refinement
1173 reflections	$\Delta\rho_{max} = 0.61$ e Å^{-3}
87 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H4···O2	0.86 (3)	2.05 (3)	2.895 (2)	165 (3)
N2—H3···O1^{ii}	0.81 (3)	2.10 (3)	2.908 (2)	177 (3)
N1—H1···O1^{iii}	0.82 (3)	2.08 (3)	2.889 (2)	175 (2)
N1—H2···O2^{iv}	0.82 (3)	2.05 (3)	2.856 (2)	167 (3)

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4 Software*; data reduction: *OpenMolEN* (Enraf–Nonius, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

References

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supplementary materials

Redetermination of bis(*S*-methylthiuronium) sulfate

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Comment

The *S*-Methyl-thiuronium cation exhibits an almost planar thiourea-unit (r.m.s. deviation for N1,N2,C1,S1 = 0.0004 Å), the methyl-group differs from planarity to a considerable degree (C2—S1—C1—N2 − 18.4 (2)°). In the sulfate anion the coordination of the sulfur atom by the four oxygen atoms can be considered as slightly distorted tetrahedral, with O—S—O bond angles in the range 108.79 (13)–110.64 (13)° (Fig.1).

In the crystal structure, each $C_2H_7N_2S^+$ cation is linked to two SO_4^- anions by four N—H⋯O hydrogen-bonds (Fig.2) with relatively short donor-acceptor distances (Tab.2).

Experimental

S-Methylisothiourea sulfate was synthesized in a modified literature procedure (Arndt 1921). Dimethylsulfate Me_2SO_4 (6.30 g, 49.95 mmol) was slowly added to a slurry of thiourea $(NH_2)_2CS$ (7.60 g, 99.84 mmol) in 150 ml of water. The reaction mixture was stirred for 5 min at room temperature and then heated first to 30°C for 1.5 h and afterwards to 100°C under reflux. The solvent was destilled off. The colourless crystalline residue was washed with twice the volume of the crystalline residue of a mixture consisting of ethanole and water (10:1). The mixture was stirred for 5 min, filtrated and the crystalline solid dried *in vacuo*. Yield: 12.35 g (44.36 mmol, 44.5%). Anal. calc. (found) for $C_4H_{14}N_4O_4S_3$: C 17.26 (17.14), H 5.07 (5.20), N 20.13 (20.02), S 34.56 (33.52)%. ^{1}H-NMR ($CDCl_3$, 25°C): δ = 2.41 (s, 3H, CH_3), 4.63 (s, 4 H, H_2NCNH_2). $^{13}C\{^1H\}$-NMR: δ = 172.89 (s, H_2NCNH_2), 12.96 (s, CH_3). ^{14}N-NMR: δ = − 280.22. IR (KBr, cm^{-1}): ν = 3989 w, 3903 w, 3840 w, 3799 w, 3748 w, 3736 w, 3673 w, 3650 w, 3211 *versus*, 3030 *versus*, 2802 s, 2367 ms, 2291 m, 2103 w, 2052 w, 1682 *versus* (n_{sym} C=N), 1564 s, 1438 s, 1419 s, 1321 m, 1150 s, 1127 s, 1078 s, 982 s, 732 s, 698 s, 602 s, 482 s, 429 m. Raman (200 mW, 25°C, cm^{-1}): ν = 3029 (11), 3009 (11), 2944 (33), 1678 (5) (n_{sym} C=N), 1436 (19), 1423 (16), 1326 (6), 1148 (40), 1133 (24), 1117 (31), 1075 (17), 976 (100), 733 (12), 702 (67), 603 (12), 485 (42), 431 (73), 268 (14), 146 (58). MS (FAB, 70 eV, NBA-Matrix, >5%); m/*z*: 359 (8), 91 (20) [M^+], 89 (16) [$(M − 2 H)^+$]. Crystallization from a saturated ethanole/water (10:1) solution at ambient temperature gave colourless X-ray quality crystals.

Refinement

H atoms bonded to N atoms were located in a difference map and refined freely. Other H atoms were positioned geometrically and refined using a riding model (including free rotation about the S1—C2 bond), with C—H = 0.96 Å and with U_{iso}(H) = 1.5 times U_{eq}(C).
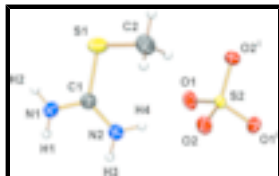
supplementary materials

Figures

Fig. 1. Molecular structure of the title compound, showing the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i) $-x + 1$, y, $-z + 1/2$.
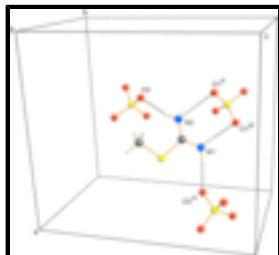

Fig. 2. Part of the packing diagram of (I). Unique N—H···O interactions represented by dashed lines are shown for one molecule of (I). Symmetry codes: (ii) $-x + 1$, $-y + 2$, $-z + 1$; (iii) x, $-y + 2$, $z + 1/2$; (iv) $x + 1/2$, $-y + 3/2$, $-z + 1$.

bis(*S*-methylthiuronium) sulfate

Crystal data

$2C_2H_7N_2S^+ \cdot SO_4^{2-}$	$F_{000} = 584$
$M_r = 278.37$	$D_x = 1.544$ Mg m^{-3}
Orthorhombic, *Pbcn*	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2n 2ab	Cell parameters from 25 reflections
$a = 11.3250$ (19) Å	$\theta = 9–18°$
$b = 8.3903$ (18) Å	$\mu = 0.62$ mm^{-1}
$c = 12.6041$ (17) Å	$T = 295$ (2) K
$V = 1197.6$ (4) Å^3	Block, colourless
$Z = 4$	$0.57 \times 0.53 \times 0.47$ mm

Data collection

Nonius MACH3 diffractometer	$R_{int} = 0.006$
Radiation source: fine-focus sealed tube	$\theta_{max} = 26.0°$
Monochromator: graphite	$\theta_{min} = 3.0°$
$T = 295(2)$ K	$h = -13 \rightarrow 0$
o–2T–scan	$k = -10 \rightarrow 0$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = 0 \rightarrow 15$
$T_{min} = 0.717$, $T_{max} = 0.749$	3 standard reflections
1175 measured reflections	every 7200 min
1173 independent reflections	intensity decay: -0.7%
1098 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.8658P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
1173 reflections	$\Delta\rho_{min} = -0.36$ e Å^{-3}
87 parameters	Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.065 (4)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
S1	0.73533 (5)	0.62211 (8)	0.47370 (5)	0.0500 (3)
N1	0.69384 (17)	0.7584 (3)	0.65367 (14)	0.0402 (5)
H1	0.660 (2)	0.820 (3)	0.694 (2)	0.043 (7)*
H2	0.760 (3)	0.722 (3)	0.666 (2)	0.049 (7)*
N2	0.54254 (16)	0.7861 (2)	0.53413 (15)	0.0341 (4)
H3	0.507 (2)	0.840 (3)	0.577 (2)	0.045 (7)*
H4	0.518 (3)	0.783 (3)	0.469 (2)	0.051 (8)*
C1	0.64701 (17)	0.7327 (2)	0.56010 (15)	0.0312 (4)
C2	0.6354 (2)	0.5513 (3)	0.37475 (19)	0.0451 (6)
H5	0.6748	0.4749	0.3305	0.054*
H6	0.6088	0.6391	0.3322	0.054*
H7	0.5688	0.5018	0.4084	0.054*
S2	0.5000	0.92901 (8)	0.2500	0.0240 (2)
O1	0.58511 (12)	1.03141 (18)	0.30668 (11)	0.0384 (4)
O2	0.43656 (12)	0.82932 (19)	0.32713 (10)	0.0358 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0339 (4)	0.0703 (5)	0.0460 (4)	0.0141 (3)	0.0011 (2)	−0.0210 (3)
N1	0.0311 (9)	0.0572 (12)	0.0322 (9)	0.0152 (9)	−0.0035 (8)	−0.0054 (8)
N2	0.0295 (9)	0.0469 (10)	0.0259 (9)	0.0075 (8)	0.0003 (7)	−0.0028 (7)
C1	0.0275 (9)	0.0376 (10)	0.0285 (9)	0.0024 (7)	0.0036 (7)	0.0017 (8)
C2	0.0492 (13)	0.0477 (12)	0.0385 (11)	0.0041 (10)	0.0003 (10)	−0.0080 (9)
S2	0.0186 (3)	0.0364 (4)	0.0170 (3)	0.000	0.0003 (2)	0.000
O1	0.0327 (7)	0.0537 (9)	0.0289 (7)	−0.0127 (7)	−0.0031 (6)	−0.0053 (6)
O2	0.0283 (7)	0.0522 (8)	0.0270 (7)	−0.0070 (6)	0.0040 (5)	0.0072 (6)

Geometric parameters (Å, °)

S1—C1	1.7459 (19)	C2—H5	0.9600
S1—C2	1.786 (2)	C2—H6	0.9600
N1—C1	1.311 (3)	C2—H7	0.9600
N1—H1	0.82 (3)	S2—O2^i	1.4699 (13)
N1—H2	0.82 (3)	S2—O2	1.4699 (13)
N2—C1	1.307 (3)	S2—O1	1.4756 (14)
N2—H3	0.81 (3)	S2—O1^i	1.4756 (14)
N2—H4	0.86 (3)		
C1—S1—C2	104.44 (10)	S1—C2—H6	109.5
C1—N1—H1	118.3 (18)	H5—C2—H6	109.5
C1—N1—H2	118.7 (19)	S1—C2—H7	109.5
H1—N1—H2	122 (3)	H5—C2—H7	109.5
C1—N2—H3	118.5 (19)	H6—C2—H7	109.5
C1—N2—H4	121.1 (19)	O2^i—S2—O2	110.64 (13)
H3—N2—H4	119 (3)	O2^i—S2—O1	109.40 (8)
N2—C1—N1	122.37 (19)	O2—S2—O1	109.29 (8)
N2—C1—S1	123.00 (16)	O2^i—S2—O1^i	109.29 (8)
N1—C1—S1	114.63 (15)	O2—S2—O1^i	109.40 (8)
S1—C2—H5	109.5	O1—S2—O1^i	108.79 (13)
C2—S1—C1—N2	−18.4 (2)	N1—N2—C1—S1	−180.0 (3)
C2—S1—C1—N1	161.61 (17)		

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H4···O2	0.86 (3)	2.05 (3)	2.895 (2)	165 (3)
N2—H3···O1^{ii}	0.81 (3)	2.10 (3)	2.908 (2)	177 (3)
N1—H1···O1^{iii}	0.82 (3)	2.08 (3)	2.889 (2)	175 (2)
N1—H2···O2^{iv}	0.82 (3)	2.05 (3)	2.856 (2)	167 (3)

Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*+1; (iii) *x*, −*y*+2, *z*+1/2; (iv) *x*+1/2, −*y*+3/2, −*z*+1.

Fig. 1

Fig. 2