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Dithiobis(formamidinium) bis(hydrogen sulfate)

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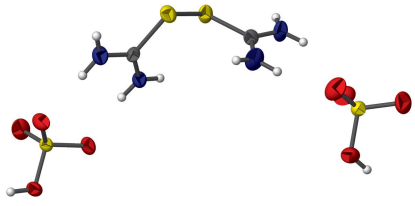
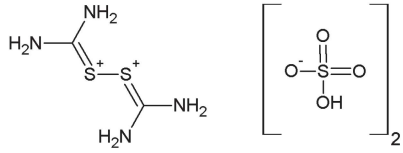
Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the title salt, dithiobis(formamidinium) bis(hydrogen sulfate), $C_2H_8N_4S_2^{2+}\cdot 2HSO_4^-$, is built up from dithiobis(formamidinium) cations and hydrogensulfate anions. The anion is an almost regular tetrahedron. In the crystal, the anions and cations are linked by O—H···O and N—H···O hydrogen bonds, generating a three-dimensional network.

3D view



Chemical scheme



Structure description

The asymmetric unit of the title compound comprises one dithiobis(formamidinium) cation and two hydrogensulfate anions (Fig. 1). The bond distances and angles in the organic cations show no significant differences from those in a related compound involving the same organic groups (Zouihri, 2012). In the sulfate anion, the S—O bond lengths range from 1.436 (2) to 1.540 (2) Å. It is worth noting that the S3—O3 and S4—O7 distances are the longest because O4 and O7 are bonded to an H atom. The construction of the three-dimensional architecture (Fig. 2) is consolidated by O—H···O and N—H···O hydrogen bonds (Table 1).

Synthesis and crystallization

Equimolar solutions of thiourea dissolved in methanol and aqueous sulfuric acid were mixed together and stirred for about 1 h. Crystals of the title compound were formed as the solvent evaporated over a few days at room temperature. They were filtered off, dried and repeatedly recrystallized as colourless prisms to enhance the purity of the product.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···O6^{i}	0.83 (2)	2.33 (3)	2.860 (3)	123 (3)
N3—H3A···O5	0.86 (2)	2.24 (2)	3.032 (3)	153 (3)
N3—H3A···O7^{ii}	0.86 (2)	2.48 (3)	3.048 (3)	125 (3)
N1—H1A···O4	0.85 (2)	2.03 (2)	2.866 (3)	170 (3)
N1—H1B···O4^{iii}	0.85 (2)	2.14 (3)	2.813 (3)	136 (3)
N3—H3B···O2^{iv}	0.85 (2)	2.02 (2)	2.861 (3)	173 (3)
N2—H2A···O5^{v}	0.85 (2)	2.03 (2)	2.868 (3)	169 (3)
N2—H2B···O1	0.86 (2)	2.10 (2)	2.955 (3)	172 (3)
O3—H3···O1^{vi}	0.84 (2)	1.79 (2)	2.628 (2)	175 (5)
N4—H4B···O6	0.86 (2)	1.97 (2)	2.815 (3)	168 (4)
O7—H7···O8^{vii}	0.85 (2)	1.76 (2)	2.602 (3)	168 (5)
N4—H4A···O6^{i}	0.83 (2)	2.33 (3)	2.860 (3)	123 (3)
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O7—H7···O8^{vii}	0.85 (2)	1.76 (2)	2.602 (3)	168 (5)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+2, -y+1, -z+1$; (v) $x, y-1, z$; (vi) $-x, -y, -z+1$; (vii) $-x+1, -y+2, -z$.

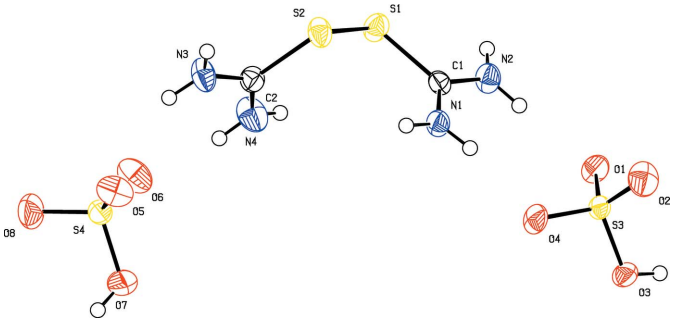

Figure 1
Molecular view of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

References

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Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zouihri, H. (2012). *Acta Cryst.* E**68**, o257.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_2H_8N_4S_2^{2+}\cdot 2HO_4S^-$
M_r	346.38
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	5.1371 (2), 9.5237 (4), 12.9884 (6)
α, β, γ (°)	106.521 (2), 96.067 (2), 95.618 (2)
V (Å^3)	600.32 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.83
Crystal size (mm)	0.21 × 0.17 × 0.12
Data collection	
Diffractometer	Bruker X8 APEXII CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.844, 0.905
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14082, 2892, 2625
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.100, 1.11
No. of reflections	2892
No. of parameters	203
No. of restraints	10
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.53

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

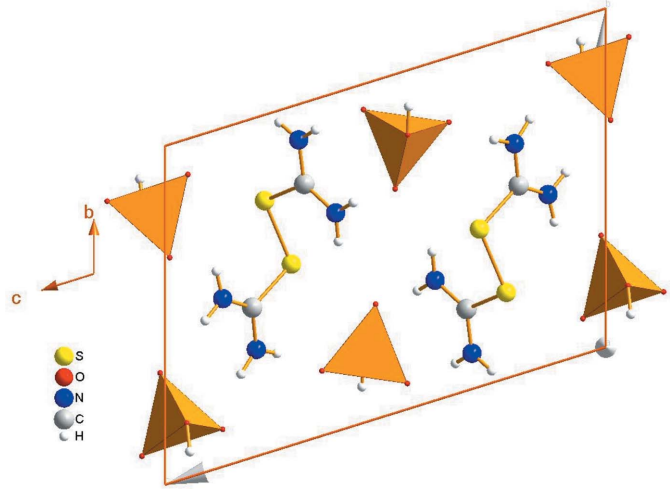

Figure 2
Packing of the title compound. HSO_4^- anions are drawn as tetrahedra.

full crystallographic data

IUCrData (2018). **3**, x181540 [https://doi.org/10.1107/S2414314618015407]

Dithiobis(formamidinium) bis(hydrogen sulfate)

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Dithiobis(formamidinium) bis(hydrogen sulfate)

Crystal data

$C_2H_8N_4S_2^{2+}\cdot 2HO_4S^-$
M_r = 346.38
Triclinic, $P\overline{1}$
a = 5.1371 (2) Å
b = 9.5237 (4) Å
c = 12.9884 (6) Å
α = 106.521 (2)°
β = 96.067 (2)°
γ = 95.618 (2)°
V = 600.32 (4) Å^3
Z = 2
$F(000)$ = 356
D_x = 1.916 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 278 reflections
θ = 1.2–31.2°
μ = 0.83 mm^{-1}
T = 293 K
Prism, colourless
0.21 × 0.17 × 0.12 mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.844, T_{max} = 0.905
14082 measured reflections
2892 independent reflections
2625 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 28.0°, θ_{min} = 3.2°
h = −6→6
k = −12→12
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.100
S = 1.11
2892 reflections
203 parameters
10 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.7302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Special details

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

Refinement. H atoms were located from a difference map and were allowed to refine with O—H and N—H restrained to 0.86 (2) Å.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S3	0.22662 (11)	0.20042 (6)	0.54402 (4)	0.02342 (14)
S4	0.65664 (11)	0.82235 (6)	0.03004 (5)	0.02686 (14)
S1	0.98932 (13)	0.25348 (7)	0.22595 (5)	0.03335 (16)
S2	1.16936 (12)	0.46501 (7)	0.28680 (5)	0.03345 (16)
O3	−0.0718 (3)	0.19092 (19)	0.55064 (15)	0.0307 (4)
O6	0.6665 (5)	0.6659 (2)	−0.01074 (18)	0.0465 (5)
O1	0.2632 (4)	0.07584 (18)	0.45047 (15)	0.0346 (4)
O4	0.2952 (4)	0.33873 (18)	0.52202 (16)	0.0368 (4)
N2	0.6532 (5)	0.1055 (2)	0.30371 (18)	0.0327 (5)
O5	0.8279 (4)	0.8898 (2)	0.13095 (16)	0.0428 (5)
O2	0.3620 (4)	0.1912 (2)	0.64396 (17)	0.0461 (5)
N3	1.1645 (5)	0.6848 (3)	0.20735 (19)	0.0372 (5)
N1	0.6973 (4)	0.3550 (2)	0.38724 (18)	0.0298 (4)
O7	0.3693 (4)	0.8386 (3)	0.0499 (2)	0.0522 (6)
N4	0.8166 (5)	0.5039 (3)	0.1312 (2)	0.0454 (6)
O8	0.7077 (5)	0.8946 (3)	−0.05202 (18)	0.0538 (6)
C2	1.0307 (5)	0.5578 (3)	0.19805 (19)	0.0283 (5)
C1	0.7569 (5)	0.2408 (2)	0.31604 (18)	0.0250 (4)
H4A	0.744 (6)	0.418 (2)	0.117 (3)	0.047 (10)*
H3A	1.112 (6)	0.743 (3)	0.173 (2)	0.039 (8)*
H1A	0.585 (5)	0.340 (3)	0.427 (2)	0.027 (7)*
H1B	0.767 (6)	0.442 (2)	0.394 (3)	0.041 (9)*
H3B	1.303 (5)	0.715 (4)	0.254 (2)	0.051 (10)*
H2A	0.710 (6)	0.036 (3)	0.259 (2)	0.040 (8)*
H2B	0.530 (5)	0.091 (4)	0.341 (2)	0.042 (9)*
H3	−0.139 (9)	0.108 (3)	0.553 (4)	0.087 (15)*
H4B	0.749 (8)	0.553 (4)	0.091 (3)	0.073 (13)*
H7	0.329 (9)	0.925 (3)	0.057 (4)	0.081 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S3	0.0233 (3)	0.0185 (2)	0.0279 (3)	−0.00014 (18)	0.0047 (2)	0.0066 (2)
S4	0.0270 (3)	0.0264 (3)	0.0278 (3)	0.0039 (2)	0.0031 (2)	0.0091 (2)
S1	0.0396 (3)	0.0294 (3)	0.0326 (3)	0.0053 (2)	0.0146 (3)	0.0081 (2)
S2	0.0308 (3)	0.0365 (3)	0.0343 (3)	−0.0032 (2)	−0.0046 (2)	0.0182 (3)
O3	0.0252 (8)	0.0272 (8)	0.0410 (10)	0.0020 (7)	0.0101 (7)	0.0110 (7)
O6	0.0561 (13)	0.0266 (9)	0.0483 (12)	0.0042 (8)	−0.0073 (10)	0.0035 (8)
O1	0.0395 (10)	0.0209 (8)	0.0425 (10)	0.0032 (7)	0.0172 (8)	0.0040 (7)
O4	0.0423 (10)	0.0188 (8)	0.0522 (11)	0.0004 (7)	0.0196 (9)	0.0120 (7)
N2	0.0431 (12)	0.0221 (10)	0.0320 (11)	0.0024 (9)	0.0103 (9)	0.0057 (8)
O5	0.0462 (11)	0.0388 (10)	0.0338 (10)	0.0094 (9)	−0.0043 (8)	−0.0021 (8)
O2	0.0399 (11)	0.0582 (13)	0.0386 (11)	−0.0044 (9)	−0.0085 (8)	0.0207 (10)
N3	0.0403 (13)	0.0347 (11)	0.0361 (12)	−0.0055 (9)	−0.0085 (10)	0.0183 (10)
N1	0.0386 (12)	0.0211 (9)	0.0327 (11)	0.0069 (8)	0.0135 (9)	0.0086 (8)

O7	0.0286 (10)	0.0588 (14)	0.0850 (17)	0.0120 (9)	0.0161 (10)	0.0416 (13)
N4	0.0394 (13)	0.0433 (14)	0.0488 (15)	−0.0068 (11)	−0.0173 (11)	0.0188 (12)
O8	0.0746 (16)	0.0570 (13)	0.0477 (12)	0.0240 (12)	0.0308 (11)	0.0312 (11)
C2	0.0271 (11)	0.0331 (12)	0.0252 (11)	0.0022 (9)	0.0011 (9)	0.0109 (9)
C1	0.0286 (11)	0.0246 (10)	0.0239 (10)	0.0065 (8)	0.0028 (8)	0.0100 (8)

Geometric parameters (Å, º)

S3—O2	1.436 (2)	N2—H2A	0.846 (18)
S3—O4	1.4441 (17)	N2—H2B	0.861 (18)
S3—O1	1.4803 (18)	N3—C2	1.299 (3)
S3—O3	1.5397 (18)	N3—H3A	0.858 (18)
S4—O5	1.4393 (19)	N3—H3B	0.849 (18)
S4—O6	1.440 (2)	N1—C1	1.298 (3)
S4—O8	1.456 (2)	N1—H1A	0.847 (17)
S4—O7	1.540 (2)	N1—H1B	0.845 (18)
S1—C1	1.777 (2)	O7—H7	0.851 (19)
S1—S2	2.0282 (9)	N4—C2	1.289 (3)
S2—C2	1.774 (2)	N4—H4A	0.828 (18)
O3—H3	0.840 (19)	N4—H4B	0.859 (19)
N2—C1	1.304 (3)		
O2—S3—O4	114.18 (13)	H2A—N2—H2B	123 (3)
O2—S3—O1	111.76 (13)	C2—N3—H3A	123 (2)
O4—S3—O1	109.77 (11)	C2—N3—H3B	119 (2)
O2—S3—O3	108.85 (12)	H3A—N3—H3B	118 (3)
O4—S3—O3	104.91 (11)	C1—N1—H1A	117.7 (19)
O1—S3—O3	106.89 (10)	C1—N1—H1B	122 (2)
O5—S4—O6	112.33 (12)	H1A—N1—H1B	121 (3)
O5—S4—O8	112.41 (15)	S4—O7—H7	114 (3)
O6—S4—O8	110.66 (14)	C2—N4—H4A	124 (2)
O5—S4—O7	108.55 (14)	C2—N4—H4B	121 (3)
O6—S4—O7	105.97 (14)	H4A—N4—H4B	114 (4)
O8—S4—O7	106.52 (13)	N4—C2—N3	123.5 (2)
C1—S1—S2	103.40 (8)	N4—C2—S2	122.9 (2)
C2—S2—S1	104.56 (9)	N3—C2—S2	113.63 (18)
S3—O3—H3	113 (3)	N1—C1—N2	123.5 (2)
C1—N2—H2A	118 (2)	N1—C1—S1	123.21 (18)
C1—N2—H2B	119 (2)	N2—C1—S1	113.31 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*+1, *y*, *z*; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+2, −*y*+1, −*z*+1; (v) *x*, *y*−1, *z*; (vi) −*x*, −*y*, −*z*+1; (vii) −*x*+1, −*y*+2, −*z*.