static interaction. Indeed, all H atoms on the N4*S* atom are involved in hydrogen bonding with atoms of other anions.

Experimental

Compound (I) was prepared by refluxing benzene-1,2,4,5-tetracarboxylic anhydride (2 g, 11.7 mmol; Aldrich) and hydrazine hydrate (25 equivalents) in dry dimethylformamide (100 ml) for 12 h under nitrogen. The solvent was removed and recrystallization of the crude product from a water–methanol mixture (*ca* 1:4) afforded a yellow solid [^{1}H NMR (d_6-DMSO): δ 6.18 (*s*, 4H), 8.34 (*s*, 6H), 8.83 p.p.m. (*s*, 2H)]. Slow vapour diffusion of methanol into a saturated solution of the compound in water afforded yellow crystals suitable for X-ray crystallography.

Crystal data

$2N_2H_5^+ \cdot C_{10}H_4N_2O_6^{2-}$
M_r = 314.27
Monoclinic
$C2/c$
a = 25.300 (5) Å
b = 7.366 (2) Å
c = 14.609 (3) Å
β = 113.62 (3)°
V = 2494.4 (9) Å^3
Z = 8
D_x = 1.674 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 606 reflections
θ = 10.2–20.8°
μ = 0.140 mm^{-1}
T = 100 (2) K
Plate
0.32 × 0.18 × 0.03 mm
Light yellow

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.957, T_{max} = 0.996
14 694 measured reflections
3496 independent reflections

2443 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 29.96°
$h = -35 \rightarrow 34$
$k = -10 \rightarrow 10$
$l = -19 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.107
S = 1.035
3496 reflections
255 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.50P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.392 e Å^{-3}
$\Delta\rho_{min}$ = −0.285 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O2^{i}	0.82 (2)	1.86 (2)	2.645 (2)	160 (2)
N3—H3N···N1*S*	0.83 (2)	2.11 (2)	2.928 (2)	168 (2)
N1*S*—H11*S*···O5^{ii}	0.89 (2)	2.17 (2)	2.996 (2)	154 (2)
N1*S*—H12*S*···O5^{iii}	0.87 (2)	2.44 (2)	3.134 (2)	137 (2)
N2*S*—H21*S*···O4^{iv}	0.98 (2)	1.81 (2)	2.790 (2)	175 (2)
N2*S*—H22*S*···O6^{iii}	0.99 (2)	1.99 (2)	2.831 (2)	141 (2)
N2*S*—H23*S*···O3^{v}	0.98 (2)	1.87 (2)	2.838 (2)	168 (2)
N3*S*—H31*S*···O2^{vi}	0.93 (2)	2.07 (2)	2.940 (2)	154 (2)
N3*S*—H32*S*···O4^{vii}	0.94 (2)	2.08 (2)	3.002 (2)	168 (2)
N4*S*—H41*S*···O3^{i}	0.97 (2)	1.85 (2)	2.808 (2)	169 (2)
N4*S*—H42*S*···N2^{v}	0.95 (2)	2.08 (2)	3.027 (2)	170 (2)
N4*S*—H43*S*···O5^{viii}	0.97 (2)	1.81 (2)	2.763 (2)	167 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, 2-y, -z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, \frac{5}{2}-y, z-\frac{1}{2}$; (v) $-x, y, \frac{1}{2}-z$; (vi) $-x, y-1, \frac{1}{2}-z$; (vii) $x, 2-y, \frac{1}{2}+z$; (viii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$.

All H atoms were located from difference Fourier maps and were refined isotropically without constraints.

Data collection: *SMART* (Bruker, 1998). Cell refinement: *SMART*. Data reduction: *SAINT-Plus* (Bruker, 1998). Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *SHELX*97. Software used to prepare material for publication: *SHELX*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1312). Services for accessing these data are described at the back of the journal.

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1-Hydroxy-2(1*H*)-pyridinethione

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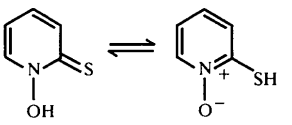
Abstract

1-Hydroxy-2(1*H*)-pyridinethione, C_5H_5NOS, crystallizes as the thione tautomer, with an intramolecular hydrogen bond between the hydroxyl and thione groups. C—H···O bonds link the molecules into centrosymmetric dimers which form a three-dimensional network *via* C—H···S interactions.

Comment

1-Hydroxypyridine-2(1*H*)-thione [pyrithione, (I)] has been widely studied due mostly to its useful antimicrobial activity. Pyrithiones are commonly used to prevent biodeterioration in aqueous functional fluids including adhesives, latex paints and cosmetics (Paulus, 1993). Although there have been numerous studies concerning metal complexes of (I) (Robinson, 1964); Barnett *et al.*, 1977; Xu *et al.*, 1995), no crystallographic information has yet been reported for pyrithione itself. This is somewhat surprising since the solid-state structure of the material influences relevant physicochemical properties such as thermal stability and solubility.

In solution, pyrithione exists in two tautomeric forms: 1-hydroxypyridine-2-thione, (I*a*), and 2-mercaptopyridine-*N*-oxide, (I*b*). Jones & Katritsky (1960) have established by UV and IR spectroscopy that the thione form is the predominant one. The crystal structure of (I) shows that the thione form is also adopted in the solid state.



(I*a*) (I*b*)

The N—O and C—S bond distances in (I) compare with average distances (Allen *et al.*, 1987) for N—O single and C=S double bonds [N1—O1 1.373 (2) *cf.* N—O_{ave} 1.396 (12) Å; C1—S1 1.693 (2) *cf.* C=S_{ave} 1.671 (24) Å]. The location of H1 in a difference Fourier map confirms the presence of the hydroxyl group. H1 is involved in an intramolecular hydrogen bond to the thione group [H1···S1 2.15 (2) Å and O1—H1···S1 132.1 (19)°] and so cannot become involved in intermolecular hydrogen bonding. As a result, the crystal structure of (I) contains only weak intermolecular interactions.

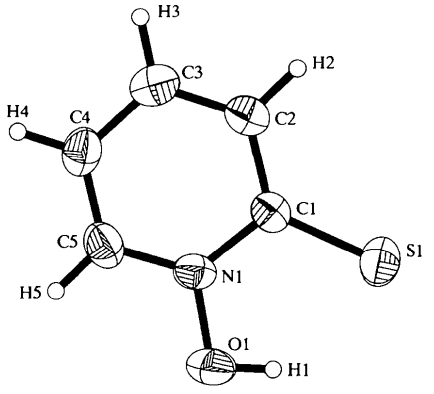


Fig. 1. The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.

The molecular units are joined *via* pairs of equivalent C—H···O interactions [C5···O1^{i} 3.343 (6) Å and C5—H5···O1^{i} 156.8°; symmetry code: (i) $1-x, -y, 1-z$] into centrosymmetric dimers which pack in a herring-bone arrangement. Short S···H contacts suggest the existence of additional weak C—H···S interactions [C3···S1^{ii} 3.681 (3) Å and C3—H3···S1^{ii} 141.2°; symmetry code: (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$] which link the dimers into a three-dimensional network.

Experimental

The sample of (I) was obtained from Aldrich Chemical Company and single crystals were grown from a solution in ethyl acetate.

Crystal data

C_5H_5NOS
M_r = 127.16
Monoclinic
$P2_1/n$
a = 6.231 (3) Å
b = 7.935 (4) Å
c = 11.667 (6) Å
β = 92.09 (3)°
V = 576.5 (5) Å^3
Z = 4
D_x = 1.465 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 18.0–21.8°
μ = 0.447 mm^{-1}
T = 180 (2) K
Block
0.30 × 0.20 × 0.20 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–θ scans
Absorption correction: none
1799 measured reflections
1014 independent reflections
695 reflections with $I > 2\sigma(I)$

R_{int} = 0.025
θ_{max} = 24.98°
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 13$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.086
S = 1.016
1014 reflections
77 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.1936P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.011
$\Delta\rho_{max}$ = 0.176 e Å^{-3}
$\Delta\rho_{min}$ = −0.223 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

All H atoms on the ring were riding with C—H = 0.95 Å and U(H) = 1.2U_{eq}(C). H1, associated with the hydroxyl group, was located in a difference Fourier map and refined with a fixed U_{iso} of 0.05 Å^2.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1307). Services for accessing these data are described at the back of the journal.

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The oxidized form of glutathione

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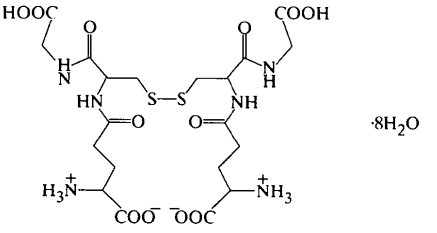
Abstract

The crystal structure of the oxidized form of the tripeptide glutathione (γ-L-glutamyl-L-cystylglycine octahydrate, $C_{20}H_{32}N_6O_{12}S_2\cdot 8H_2O$) has been determined at 100 K. The molecule was crystallized from aqueous solution in the presence of the precipitating agent polyethylene glycol by the vapor-diffusion method, which is commonly used in protein crystallization. The space group is $P2_12_12$ and the molecule contains a crystallographic twofold symmetry axis through the middle of the disulfide bridge. There are four water molecules per tripeptide, two of which are disordered. The S—S and S—C bond lengths are 2.0387 (9) and 1.8098 (19) Å, respectively, and the C—S—S bond angle is 105.03 (6)°.

Comment

The reduced form of glutathione (GSH) is present in animal cells and has various biological functions, notably the reduction of toxic peroxides. The SH group can be oxidized to form a disulfide bridge: 2GSH → GSSG + 2[H] (Metzler, 1977). The crystal structure of the reduced form of glutathione has been determined by Wright (1958) and redetermined by Görbitz (1987). The tripeptide glutathione (γ-L-glutamyl-L-cystylglycine) has a special peptide linkage as the glutamic acid residue is attached to the cystine residue through the γ-carboxyl group rather than through the α-carboxyl group.

The structure of $GSSG\cdot 8H_2O$ has been determined using orthorhombic crystals of space group $P2_12_12$. The crystal structure contains a crystallographic



GSSG

twofold symmetry axis through the center of the disulfide bridge (Fig. 1). There are four water molecules in the asymmetric unit and two of them are disordered. The stereochemical data for the side chain of the cystine residue and the disulfide bridge are given in Table 1. The glutathione peptide has a left-handed disulfide chirality [C—S—S—C = −97.0 (4)°], unlike cystine in the tetragonal (Chaney & Steinrauf, 1974) and hexagonal (Oughton & Harrison, 1959) crystal forms. The disulfide bridge length is 2.0387 (9) Å, which is the same, within experimental error, as the length found in tetragonal (2.043 Å) and hexagonal (2.032 Å) cystine crystals, and the mean value of 2.029 Å for 46 disulfides found in small molecules (Allen *et al.*, 1987). The C—S distance of 1.8098 (19) Å agrees also with the average value of 1.815 Å given in *International Tables for Crystallography* (Vol. C, 1992). The φ, ψ and ω