Table 4. *Hydrogen bridges found in ammonium hydrogen malate*

See Fig. 3 for the placing of the molecules.

D–H···*A*	Molecule	*D*···*A*	H···*A*	*D*–H···*A*
O(5)–H(51)···O(2)	(1)	2·58 Å	1·59 Å	169·2°
O(1)–H(11)···O(4)	(2)	2·79	1·93	171·0
N–H(41)···O(2)	(2)	2·84	1·62	160·8
N–H(42)···O(3)	(1)	2·81	1·98	167·3
N–H(43)···O(1)	(1)	2·88	2·10	157·7
N–H(44)···O(3)	(4)	2·85	2·04	148·2

involving the most acidic H atom is 'short', whereas the others are 'long'.

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S-Nitroso-*N*-acetyl-DL-penicillamine

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Abstract. $C_7H_{12}N_2O_4S$, 2-acetamido-3-methyl-3-thionitrosobutanoic acid, space group $P2_1/c$, a = 6·9840 (11), b = 12·698 (2), c = 12·353 (2) Å, β = 107·80 (1)° at 295 K (λ = 1·54051 Å), Z = 4, D_x = 1·403, D_m = 1·398 g cm^{-3}, M_r = 220·25. Thionitrite bond distances [C–S 1·833 (1), S–N 1·763 (2), N–O 1·199 (2) Å] and angles [C–S–N 100·80 (7), S–N–O 113·99 (11)°] are consistent with its description as C–S–N=O. Each thionitrite molecule participates in four intermolecular H bonds which form two-dimensional networks approximately parallel to the *bc* plane.

Introduction. Prismatic crystals formed when water was allowed to diffuse into a saturated solution of *N*-acetyl-DL-penicillamine thionitrite in methanol. The apparent color of the crystals varies with increasing crystal thickness from pale green to reddish in transmitted sunlight. Precession photographs show $2/m$ Laue symmetry with systematic absences for $h0l$ (l odd) and $0k0$ (k odd), establishing the space group as $P2_1/c$. Crystal density was determined by flotation in a mixture of chloroform and *n*-heptane. For data collection a crystal cut perpendicular to [010] (dimensions 0·53 × 0·66 × 0·47 mm, volume 0·168 mm^3) was mounted on a four-circle automated diffractometer with φ approximately parallel to [010], the longest dimension. Resolved Cu $K\alpha_1$ peaks for 28 reflections in the range $83 < 2\theta < 89°$ gave the cell constants (least-squares fit to the 2θ, ω, χ values). Intensity data for 8104 reflections were measured by θ–2θ step scans (0·03° 2θ per step, 1 s counts with 4 s background counts, 0·001 in Nb incident beam filter and Mo $K\alpha$ radiation). The data set included $\pm h,k,\pm l$ for $30 < 2\theta < 60°$ and $\pm h,\pm k,\pm l$ for $0 < 2\theta < 30°$ with Y–Zr balanced filters for $0 < 2\theta < 12°$. As provided in the diffractometer control program (Lenhert, 1975), coincidence losses were corrected, and weak reflections rescanned a maximum of two times with 20 s background counts until $I/\sigma(I) > 15$. Total X-ray exposure (50 kV, 12 mA, take-off angle 2·7°, focal spot 15 × 0·75 mm, 24 cm tube-to-crystal distance) was 424 h during which time three monitor reflections showed an intensity decrease of 1·9%. The computer program *ORABS* (Wehe, Busing & Levy, 1962) was used to calculate absorption corrections (μ = 2·890 cm^{-1}, 5 × 5 × 5 Gaussian grid, maximum, minimum and average transmission factors; 0·878, 0·857, 0·871). Symmetry-related reflections were averaged to give 3551 F_o values (92 with $F_o < 0$ were set to zero). A more complete description of the data collection and reduction procedures is given by Miller, Lenhert & Joesten (1972).

The structure was solved by the heavy-atom method (S coordinates from a sharpened Patterson function). Refinement was by a full-matrix least-squares method with minimization of $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)$ with $\sigma(F)$ calculated from counting statistics and an experimentally determined (Miller *et al.*, 1972) instability factor (1·08%). Heavy atoms were refined anisotropically; coordinate and isotropic thermal parameter refinement converged for 9 of the 12 H atoms. A ΔF synthesis showed a ring of positive electron density, characteristic of rotational disorder, around the methyl carbon of the *N*-acetyl. The disorder was approximated by six equally spaced half-H atoms which were not refined (C—H distance 1 Å, C—C—H angle 109·5°). The isotropic extinction parameter (Zachariasen, 1968) refined to give $r^* = 0{\cdot}210 \times 10^{-4}$ cm. Refinement included the unobserved reflections [$F_o = 0$, $\sigma(F)$ as described above], and the final cycle gave a maximum shift-to-error ratio of 0·09, the standard error of an observation of unit weight, 5·33, a conventional R of 0·046, and a weighted residual $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ of 0·044. The final difference map showed maximum and minimum $\Delta\rho$ values of ±0·35 e Å^{-3}. Atomic scattering factors for S, N, C and O were from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). Anomalous dispersion factors for S were from Cromer & Liberman (1970). Except as noted above, calculations were made with a modified and updated XRAY 67 program system (Stewart, 1967) on the Xerox Sigma 7 computer at Vanderbilt. Table 1 displays the final fractional coordinates.†

Table 1. *Fractional coordinates for* $C_7H_{12}N_2O_4S$

M is the population parameter (blank implies 1·0).

	M	*x*	*y*	*z*
S		0·58277 (6)	0·16480 (3)	0·22034 (3)
O(1)		0·60582 (23)	0·25325 (12)	0·04366 (13)
O(2)		0·11759 (17)	0·30180 (8)	0·18301 (9)
O(3)		−0·03570 (15)	−0·04430 (8)	0·12578 (8)
O(4)		0·06919 (18)	−0·02569 (9)	0·31385 (8)
N(1)		0·52759 (23)	0·17853 (12)	0·07190 (13)
N(2)		0·12915 (17)	0·14573 (8)	0·10121 (9)
C(1)		0·06620 (20)	−0·00045 (10)	0·21022 (10)
C(2)		0·20622 (19)	0·09030 (10)	0·20796 (10)
C(3)		0·42612 (20)	0·05097 (10)	0·22801 (11)
C(4)		0·51825 (33)	0·01118 (19)	0·34999 (15)
C(5)		0·43878 (29)	−0·03375 (14)	0·14272 (15)
C(6)		0·09227 (20)	0·24872 (10)	0·09576 (11)
C(7)		0·02514 (25)	0·29663 (12)	−0·02024 (13)
H(1)		0·2116 (18)	0·1401 (10)	0·2670 (11)
H(2)		0·1067 (20)	0·1135 (11)	0·0415 (12)
H(3)		0·0146 (30)	−0·0810 (17)	0·3145 (17)
H(41)		0·4427 (25)	−0·0491 (14)	0·3627 (13)
H(42)		0·6540 (28)	−0·0089 (14)	0·3606 (14)
H(43)		0·5092 (26)	0·0632 (16)	0·4008 (16)
H(51)		0·3723 (23)	−0·0139 (12)	0·0675 (15)
H(52)		0·5750 (27)	−0·0500 (13)	0·1490 (13)
H(53)		0·3715 (25)	−0·0961 (15)	0·1560 (14)
H(71)	0·50	0·1227	0·3500	−0·0288
H(72)	0·50	0·1265	0·2831	−0·0607
H(73)	0·50	0·0117	0·2398	−0·0795
H(74)	0·50	−0·1069	0·2634	−0·0664
H(75)	0·50	−0·1107	0·3304	−0·0344
H(76)	0·50	0·0041	0·3737	−0·0157

Discussion. Most thionitrites decompose with half-lives from a few seconds to a few hours; in contrast the thionitrite of *N*-acetyl-DL-penicillamine is atypically stable (Field, Dilts, Ravichandran, Lenhert & Carnahan, 1978). This stability allows us to report the first precision determination of the thionitrite structural parameters. Interest in *S*-nitroso-*N*-acetyl-DL-penicillamine is enhanced by extensive study of penicillamine and its *N*-acetyl derivative in antibiotic synthesis, metal chelation, and pharmacological applications. Fig. 1 defines the atomic numbering and shows the conformation adopted by $C_7H_{12}N_2O_4S$.

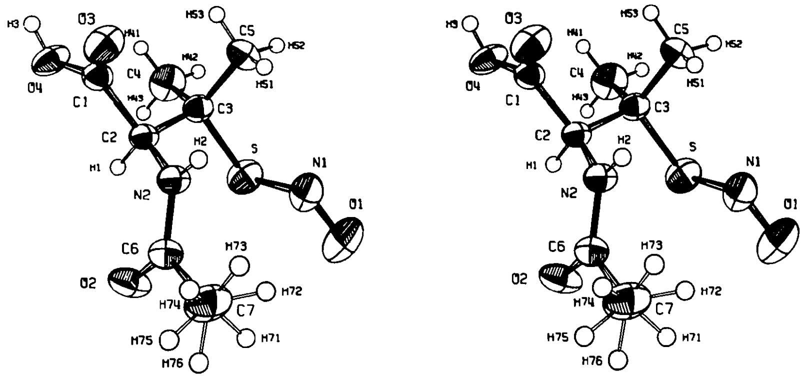

Fig. 1. Molecular conformation, numbering and thermal motion (50% probability level). Stereo by *ORTEP* (Johnson, 1965).

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33559 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

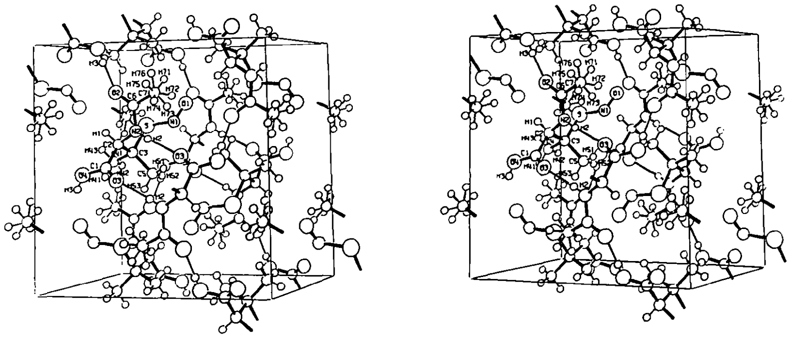

Fig. 2. Molecular packing and hydrogen bonds. Unit-cell outline with origin at the lower left rear corner; *b* vertical, *c* horizontal. Stereo by *ORTEP* (Johnson, 1965).

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

S—N(1)	1·763 (2)	S—N(1)—O(1)	113·99 (11)
O(1)—N(1)	1·199 (2)	C(3)—S—N(1)	100·80 (7)
O(2)—C(6)	1·237 (2)		
O(3)—C(1)	1·204 (1)	S—C(3)—C(2)	108·26 (9)
O(4)—C(1)	1·313 (2)	S—C(3)—C(4)	103·47 (10)
		S—C(3)—C(5)	111·02 (12)
N(2)—C(2)	1·446 (2)		
N(2)—C(6)	1·331 (2)	C(2)—C(3)—C(4)	111·02 (14)
		C(2)—C(3)—C(5)	112·18 (11)
C(1)—C(2)	1·517 (2)	C(4)—C(3)—C(5)	110·53 (13)
C(2)—C(3)	1·561 (2)	C(3)—C(2)—C(1)	111·25 (10)
C(3)—C(4)	1·532 (2)	C(3)—C(2)—N(2)	111·99 (12)
C(3)—C(5)	1·527 (2)	C(2)—N(2)—C(6)	122·48 (11)
C(3)—S	1·833 (1)	C(2)—C(1)—O(3)	123·29 (12)
C(6)—C(7)	1·494 (2)	C(2)—C(1)—O(4)	112·63 (10)
N(2)—O(3′)	2·971 (1)	O(3)—C(1)—O(4)	124·07 (13)
H(2)···O(3′)	2·16 (1)	N(2)—C(6)—O(2)	121·16 (12)
N(2)—H(2)	0·82 (1)	N(2)—C(6)—C(7)	116·61 (12)
		O(2)—C(6)—C(7)	122·21 (11)
O(2)—O(4″)	2·556 (2)		
H(3)···O(2″)	1·76 (2)	N(2)—H(2)···O(3′)	174 (1)
O(4)—H(3)	0·80 (2)	O(4)—H(3)···O(2″)	177 (2)

Symmetry code
′ $(\bar{x},\bar{y},\bar{z})$.
″ $(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z]$.

Table 2 displays interatomic distances and angles. Although no structural parameters are available for other thionitrites, comparison of bond distances with similar moieties is possible.

The C—S bond length of 1·833 (1) Å observed in this structure exceeds the average C—SCH_3 length of 1·811 (4) Å for various methionine structures reported by Chen & Parthasarathy (1977). But it is less than the C—S lengths reported for two aliphatic disulfides: 1·865 (6) and 1·866 (7) Å in D-penicillamine disulfide dihydrochloride (Rosenfield & Parthasarathy, 1975) and 1·852 (8) and 1·858 (8) Å in *meso*-penicillamine disulfide dihydrate (Warner, Ottersen & Seff, 1974).

The observed S—N distance of 1·763 (2) Å found in the thionitrite indicates a single bond comparable to the 1·775 Å (neutron result) found for the single S—N bond in the zwitterionic configuration of sulfamic acid (Bats, Coppens & Koetzle, 1977).

The N=O bond length of 1·199 (2) Å contrasts with the values of 1·340 (1), 1·276 (2), 1·282 (1) and 1·234 (2) Å found by Talberg (1977*a*,*b*, and references therein) in aromatic *C*-nitroso compounds for N—O bonds intermediate between single and double bond order.

The other distances and angles of the penicillamine moiety, although showing substantially increased precision, are comparable to those observed in the two penicillamine disulfide structures cited above.

The *N*-acetyl, carboxyl, and thionitrite moieties are planar. The carboxyl H is displaced from the carboxyl least-squares plane by 0·2 Å. The carboxyl and thionitrite planes form a dihedral angle of 4·5°, while they subtend angles of 50·3 and 46·9° respectively with the *N*-acetyl plane.

The packing and intermolecular H bonds are shown in Fig. 2, and the H bonds are summarized in Table 2. Individual molecules are bound into dimers by two H bonds, N(2)—H(2)···O(3), across an inversion center. These dimers are then linked into a network approximately parallel to the *bc* plane by H bonds, O(4)—H(3)···O(2), to two adjacent molecules. This pattern of H bonding conforms to that described for *N*-acyl amino acids and peptides in the survey of crystal structures by Chen & Parthasarathy (1978). All other intermolecular contacts are consistent with normal van der Waals distances. Note that the thionitrite moieties are sequestered in an apolar environment between two adjacent H-bonded networks, a feature which may contribute to the stability of the molecule in the solid state.

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Structure of Fortimicin B

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Abstract. *O*-α-D-2,6-Diamino-6-methyl-2,3,4,6-tetradeoxyglucopyranosyl-(1 → 4)-L-3-amino-1-methoxy-6 methylamino-1,3,6-trideoxy-*chiro*-inositol, $C_{15}H_{31}N_4O_5.3\cdot5H_2O$, M_r = 347·438, orthorhombic, $P2_12_12_1$, a = 13·966 (2), b = 16·472 (2), c = 9·522 (1) Å, Z = 4, D_x = 1·245 g cm^{-3}. The structure was solved by direct methods. The final R value was 0·078 for 1713 reflexions. The two six-membered rings are in the chair conformation and are bound through the α-linkage. The solvent molecules are hydrogen bonded to each other and to the molecule.

Introduction. Fortimicin B is a member of the fortimicins, which are potent broad-spectrum aminocyclitol antibiotics produced by a strain of *Micromonospora olivoasterospona* (Nara *et al.*, 1977; Okachi *et al.*, 1977). X-ray structure determination of the title molecule was carried out in order to confirm the structure proposed from chemical and spectroscopic evidence (Egan *et al.*, 1977) and to determine the absolute configuration unequivocally.

Fortimicin B was recrystallized from a methanol solution containing a trace of water. A crystal with dimensions 0·5 × 0·4 × 0·3 mm was used, sealed in a glass capillary. The precise lattice constants and intensity data were obtained from measurements on a Rigaku computer-controlled four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation. All reflexions within the range of $2\theta \leq 50°$ were collected by use of the θ–2θ scan mode with a scanning rate of 4° min^{-1}. Stationary background counts were accumulated for 10 s before and after each scan. A total of 2201 independent reflexions were obtained, of which 1713 were non-zero reflexions [$|F_o| \geq 3\cdot0\sigma(|F|)$]. No correction was made for absorption [μ(Mo $K\alpha$) = 1·082 cm^{-1}]. The phases for 436 reflexions with $|E| \geq$