Discussion. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.* Fig. 1, drawn with ORTEP (Johnson, 1965), illustrates the molecular geometry.

The diazaadamantanone molecule is protonated at only one of its N atoms, N(3), and the salt presents an example of the hydrogensulfate ion HSO_4^-. The S—OH bond length is 1·549 (3) Å and the S=O bond lengths are 1·428–1·447 (4), mean 1·437 (8) Å. In both 3-phenoxypyridinium hydrogensulfate (Bandoli et al., 1988) and 3,7-dimethyl-1,5-diphenyl-3-aza-7-azoniabi-cyclo[3.3.1]nonan-9-one hydrogensulfate (Levina et al., 1982) the hydrogen atom of the HSO_4^- anion is disordered over two oxygen sites and the apparent S—OH bond lengths of 1·502, 1·504 Å in the former and 1·473, 1·498 Å in the latter are effectively averages of S—OH and S=O distances. The mean apparent S—OH distance in these salts, 1·494 Å, is in excellent agreement with the mean of 1·549 (S—OH) and 1·437 Å (S=O) from the diazaadamantanone salt, viz. 1·493 Å.

The $C(sp^3)$—N^+ bond lengths at N(3) in the diazaadamantanone cation are 1·490–1·534 (4), mean 1·508 (19) Å, whereas the $C(sp^3)$—N bond lengths at the tertiary N atom, N(1), are 1·419–1·473 (4), mean 1·452 (23) Å. This distinct difference between bond lengths at N^+ and N was noted many years ago in the

crystal structures of alkaloids (e.g. Hamilton, Hamor, Robertson & Sim, 1962). The mean $C(sp^3)$—$C(sp^3)$ and $C(sp^3)$—$C(sp^2)$ bond lengths in the diazaadamantanone cation are 1·552 (5) and 1·528 (7) Å, respectively. The phenyl C—C distances are 1·362 (8)–1·394 (7), mean 1·385 (10) Å.

The hydrogen bonds in the crystal are N(3)H⋯O(3) ($x, y, 1+z$), 2·799 (4) Å, and O(2)H⋯O(5) ($\frac{3}{2}-x, y, \frac{1}{2}+z$), 2·536 (4) Å. For the former, N(3)—H, H⋯O(3), and N(3)—H⋯O(3) are 1·00 (3), 2·01 (4) Å, and 135 (3)°; for the latter, O(2)—H, H⋯O(5), and O(2)—H⋯O(5) are 0·86 (4), 1·75 (5) Å, and 149 (4)°.

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Structure of the Hydrate Form of 3-Methyl-2-oxo-6,7-dihydro-3H-pyrimido-[5,4-b][1,4]thiazine-7-carboxylic Acid*

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Abstract. $C_8H_9N_3O_3S.xH_2O$ ($x = 0.862$), $M_r = 242.771$, monoclinic, $P2_1$, $a = 9.8695$ (5), $b = 9.4582$ (6), $c = 5.6773$ (4) Å, $\beta = 108.995$ (6)°, $V = 501.10$ (6) Å^3, $Z = 2$, $D_m = 1.55$ (2), $D_x = 1.609$ g cm^{-3}, $\lambda(Cu\,K\alpha_1) = 1.54056$ Å, $\mu = 28.70$ cm^{-1}, $F(000) = 253.24$, $T = 296$ (1) K, final $R(F) = 0.025$ for 955 counter reflections with $F_o^2 > 2\sigma(F_o^2)$. At the beginning of the analysis, the true absorption coefficient was not known. The value used was 28·25 cm^{-1} which is 98·4% of the true value. It is believed that this would not change the results significantly. All H atoms except those of the water molecule were located and their parameters refined. The

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zwitterion structure $NH^+-CH-COO^-$ of this compound is evidenced by the bond lengths. Both O atoms of the $-COO^-$ ion act as acceptors in $N-H\cdots O$-type hydrogen bonds with a neighboring, screw-axis-related molecule, the $O\cdots H$ lengths and $O\cdots H-N$ angles being 1·90 (4) and 1·83 (5) Å, and 168 (3) and 174 (4)°, respectively.

Introduction. It has been shown (Pal, Ghosh, Sethi, Suttle & McCloskey, 1988) that 5-chloro-2'-deoxycytidine, reported to be a minor constituent of salmon sperm DNA (Lis, McLaughlin & McLaughlin, 1974), and its methyl analog react with cysteine in aqueous K_2CO_3 to form thiazine derivatives. The methyl analog (I) has been thoroughly characterized by mass spectrometry, proton magnetic resonance, ultraviolet spectroscopy and elemental analysis (Pal, Ghosh, Sethi, Suttle & McCloskey, 1988). It was purified by recrystallization from water, and the elemental analysis indicated the presence of half a mole of water per mole of the compound. Results of an X-ray study of (I), reported here, not only reveal the structural detail but also provide additional information concerning the water content.

(I)
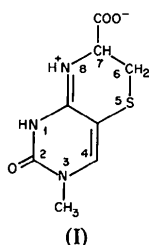
Experimental. Colorless crystals of $C_8H_9N_3O_3S.xH_2O$ were grown at room temperature from an aqueous solution. The crystal density was determined by flotation in mixtures of 2-bromobutyric acid and 1,2-dichloroethane. A crystal with dimensions 0·50 × 0·40 × 0·13 mm was mounted on a Picker diffractometer with a approximately parallel to the Φ axis of the diffractometer; lattice parameters were refined by least squares from angle measurements of 12 strong reflections in the 2θ range 90–96° (Busing, Ellison, Levy, King & Roseberry, 1968); systematic absences $0k0$, $k = 2n + 1$, consistent with $P2_1$ and $P2_1/m$. Intensity data were collected by $\theta-2\theta$ step scans in the 2θ range 1–134° ($-11 \le h \le 11$, $0 \le k \le 11$, $0 \le l \le 6$), divided into two separate subgroups based on 2θ. Within any subgroup variation for the standard reflection (600) less than 1%. In general the reflections were strong. Of the 956 independent intensities measured, only one had $F^2 < 2\sigma(F^2)$. Absorption corrections were calculated by the method of Busing & Levy (1957); the transmission range was 0·356 to 0·692. Maximum mosaic spread of the crystal used was estimated to be 0·5°.

From the fact that $D_m \simeq D_x$ (see *Abstract*) for $Z = 2$, the space group was taken to be $P2_1$. The structure was solved by the program *MULTAN* (Germain, Main & Woolfson, 1971). By iterative least-squares refinements [by the program *ORXFLS*4 (Busing, Martin & Levy, 1962)] and difference Fourier syntheses [by the program *ORFFP*3 (Levy, 1977)] all atoms of the organic molecule including nine H atoms were located and refined. The two H atoms of water could not be located conclusively and so were omitted from the refinements.

Since there was ambiguity in assigning the mole ratio of water to the compound, least-squares refinements were carried out both with the fraction of water fixed at unity and with the fraction adjusted. All refinements were based on F^2, the function minimized being $\sum w|F_o^2 - sF_c^2|^2$, where the weights w are reciprocals of $\sigma_c^2(F_o^2)^2 + (0·006F_c^2)^2$. Here σ_c is the standard error from counting statistics and s is the scale factor. The $wR(F^2)$ value obtained when the water occupancy fraction (m) was unity was 0·0823, higher than 0·0723 obtained when m was adjusted ($\mathscr{R} = 1·138$). Applying the R-factor ratio test (Hamilton, 1965), we obtained $\mathscr{R}_{1,773,0.005} = 1·005$ interpolated from Hamilton's tables for the 0·005 significance level for a one-dimensional hypothesis and 773 degrees of freedom. Hence the probability that the occupancy $m = 1$ is correct can be rejected at the 99·5% confidence level. For this reason the results obtained when m was adjusted are given in this paper. The final refinement for the correct water content [$m = 0·862$ (8)] resulted in $R(F)$, $R(F^2)$ and $wR(F^2)$ values of 0·025, 0·050 and 0·0723, respectively for 955 reflections used (data-to-variable ratio 5·25). The standard deviation of an observation of unit weight, S, was 1·283, $\Delta/\sigma_{max} = 0·78$. The final difference Fourier map showed a maximum $\Delta\rho$ of 0·19 e Å^{-3}. Scattering factors were those of Cromer & Waber (1974); anomalous-scattering correction for all non-H atoms from Cromer (1974). Because anomalous scattering is important, both configurations were refined. The configuration presented in this paper represents the absolute configuration.

Distances and angles were calculated with the program *ORFFE*4 (Busing, Martin & Levy, 1964). Figures were prepared with the program *ORTEP*II (Johnson, 1976).

Discussion. Positional parameters and isotropic temperature parameters (or their equivalents) are listed in Table 1.* The crystal structure of the compound is

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51323 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and isotropic thermal parameters for $C_8H_9N_3O_3S.xH_2O$*

The e.s.d.'s are given in all tables and in the text. The digits in parentheses correspond to the least-significant digits of the parameters. The equivalent isotropic temperature factors for non-H atoms were calculated from the corresponding anisotropic thermal parameters by the relation $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$ (Hamilton, 1959).

	x	y	z	B_{eq} or $B(\text{Å}^2)$
S	0.31306 (5)	0.25	0.28954 (7)	2.84 (2)
C(2)	0.0502 (3)	−0.0004 (3)	0.6750 (5)	3.13 (6)
C(3)	−0.1659 (3)	0.0481 (6)	0.3229 (8)	5.61 (11)
C(4)	0.0720 (3)	0.1331 (3)	0.3336 (4)	3.19 (6)
C(5)	0.2159 (2)	0.1478 (2)	0.4368 (3)	2.52 (5)
C(6)	0.4811 (2)	0.1558 (3)	0.4096 (3)	2.60 (5)
C(7)	0.5285 (2)	0.1383 (2)	0.6904 (4)	2.26 (5)
C(9)	0.2831 (2)	0.0723 (2)	0.6608 (4)	2.28 (5)
C(10)	0.5658 (2)	0.2833 (2)	0.8229 (3)	2.26 (5)
N(1)	0.1968 (2)	0.0021 (2)	0.7662 (4)	2.62 (5)
N(3)	−0.0096 (2)	0.0614 (3)	0.4452 (4)	3.58 (6)
N(8)	0.4225 (2)	0.0607 (2)	0.7673 (3)	2.30 (4)
O(1)	0.6816 (2)	0.3363 (2)	0.8204 (3)	3.48 (5)
O(2)	−0.0216 (2)	−0.0565 (2)	0.7894 (4)	4.12 (6)
O(3)	0.4802 (2)	0.3361 (2)	0.9169 (3)	3.25 (5)
OW	0.9428 (3)	0.2856 (4)	0.7557 (6)	5.77 (10)
H(1)	0.226 (3)	−0.045 (4)	0.904 (7)	3.2 (6)
H(3a)	−0.191 (4)	0.100 (6)	0.191 (7)	6.4 (12)
H(3b)	−0.192 (5)	−0.047 (5)	0.317 (9)	10.4 (20)
H(3c)	−0.202 (5)	0.103 (8)	0.444 (8)	11.3 (18)
H(4)	0.021 (3)	0.156 (4)	0.172 (6)	4.1 (6)
H(6a)	0.550 (2)	0.212 (3)	0.364 (4)	1.6 (4)
H(6b)	0.469 (3)	0.073 (4)	0.329 (5)	2.3 (5)
H(7)	0.604 (3)	0.087 (4)	0.739 (5)	2.8 (5)
H(8)	0.454 (5)	−0.011 (6)	0.882 (8)	5.7 (11)

Table 2. *Bond distances (Å) and bond angles (°) including H atoms*

N(1)—H(1)	0.87 (4)	C(4)—H(4)	0.92 (3)
C(3)—H(3a)	0.86 (4)	C(6)—H(6a)	0.96 (2)
C(3)—H(3b)	0.93 (5)	C(6)—H(6b)	0.90 (3)
C(3)—H(3c)	1.01 (5)	C(7)—H(7)	0.86 (2)
		N(8)—H(8)	0.92 (5)

H(1)—N(1)—C(2)	109 (2)	H(6a)—C(6)—C(7)	110 (1)
H(1)—N(1)—C(9)	125 (2)	H(6a)—C(6)—S	105 (1)
		H(6b)—C(6)—C(7)	113 (2)
H(3a)—C(3)—N(3)	109 (2)	H(6b)—C(6)—S	107 (2)
H(3b)—C(3)—N(3)	109 (3)	H(6a)—C(6)—H(6b)	109 (2)
H(3c)—C(3)—N(3)	100 (3)		
H(3a)—C(3)—H(3b)	121 (4)	H(7)—C(7)—N(8)	105 (2)
H(3b)—C(3)—H(3c)	112 (4)	H(7)—C(7)—C(6)	110 (2)
H(3c)—C(3)—H(3a)	104 (5)	H(7)—C(7)—C(10)	107 (2)
H(4)—C(4)—N(3)	112 (2)	H(8)—N(8)—C(7)	118 (3)
H(4)—C(4)—C(5)	124 (2)	H(8)—N(8)—C(9)	117 (3)

composed of zwitterions that are linked to neighboring, screw-axis-related molecules by forming $O(1)\cdots H(1)—N(1)$ and $O(3)\cdots H(8)—N(8)$ hydrogen bonds with $O(1)\cdots H(1)$ and $O(3)\cdots H(8)$ distances being 1.90 (4) and 1.83 (5) Å, respectively, as shown in Fig. 1. The configurations around C(6) and C(7) are tetrahedral and the configuration around N(3) is trigonal, N(3) being 0.002 (3) Å out of the plane defined by C(2), C(3) and C(4). All bond lengths and angles for non-H atoms of the compound are given in Fig. 2, and those

including H atoms are shown in Table 2. Although the chemical environments are not strictly identical, it is of interest to note that the S—C(5) distance of 1.754 (2) Å is longer than the corresponding bond distances of 1.741 (2) and 1.738 (2) Å of the five-membered ring of oltipraz (Wei, 1983) and longer than the distances 1.735 (2) and 1.701 (2) Å of its related phenyl-3*H*-1,2-dithiole-3-thione (Wei, 1986). The seven C—H and two N—H bond distances range from 0.86 (4) to 1.01 (5) Å, with an average value of 0.91 Å.
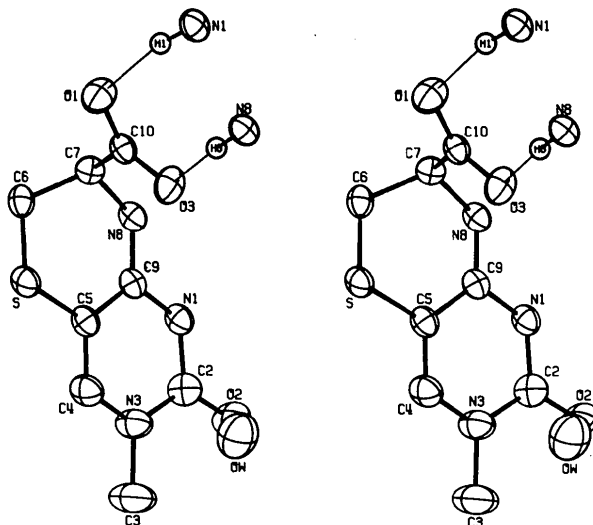

Fig. 1. A stereoscopic view of $C_8H_9N_3O_3S.xH_2O$, showing resonating $O\cdots H—N$ hydrogen bonds with a neighboring molecule. For clarity, H atoms are not shown, and thermal ellipsoids enclose 50% probability.
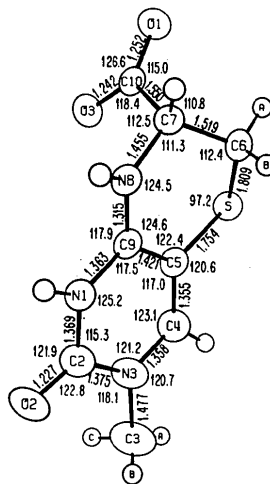

Fig. 2. Bond lengths (Å) and bond angles (°) for non-H atoms. The e.s.d.'s for bond lengths are all 0.003 Å except those for S—C(5) and S—C(6) which are 0.002 Å. The e.s.d.'s for bond angles are all 0.2° except those for C(5)—S—C(6) and S—C(6)—C(7) which are 0.3°. H atoms are numbered according to the non-H atoms to which they are bound.

Table 3. *Distances* (Å) *and angles* (°) *for the possible* H
bonds

OW···N(3ⁱ)	2·892 (4)	N(3ⁱ)–OW–N(3ⁱⁱ)	107·82 (9)
OW···N(3ⁱⁱ)	3·005 (5)	N(3ⁱ)–OW–O(1)	123·5 (1)
OW···O(1)	2·762 (4)	N(3ⁱ)–OW–O(2ⁱⁱⁱ)	151·9 (1)
OW···O(2ⁱⁱⁱ)	2·863 (4)	N(3ⁱⁱ)–OW–O(1)	103·3 (1)
		N(3ⁱⁱ)–OW–O(2ⁱⁱⁱ)	82·0 (1)
		O(1)–OW–O(2ⁱⁱⁱ)	77·34 (9)

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

The elemental analysis indicated that half a mole of water was present for one mole of the compound, while the least-squares refinements have resulted in $m = 0.862$ (8). It is well known that the structural role of a solvent is merely to occupy space in the crystal lattice or to stabilize the compound by forming weak H bonds. Examination around the water molecule reveals that it is surrounded by four N or O atoms with which hydrogen bonds could be formed. Distances and angles of these interactions are shown in Table 3.

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6-Chloro-1,2-benzodithiole-3-thione

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Abstract. $C_7H_3ClS_3$, $M_r = 218\cdot7$, monoclinic, $P2_1/a$, $a = 14\cdot427$ (3), $b = 14\cdot695$ (3), $c = 3\cdot891$ (2) Å, $\beta = 90\cdot67$ (3)°, $V = 824\cdot9$ (5) Å³, $Z = 4$, $D_x = 1\cdot76$ g cm⁻³, λ(Cu $K\alpha$) $= 1\cdot5418$ Å, $\mu = 105\cdot7$ cm⁻¹, $F(000) = 440$, room temperature, $R = 0\cdot049$ ($wR = 0\cdot052$) for 1073 observed reflections $[I > 2\sigma(I)]$. The benzodithiole skeleton is practically planar and the thione bond is clearly double.

Introduction. The title compound, which is the starting material of condensation reactions with amines, was structurally analyzed to help understand the relationship between the biological properties and structure of its derivatives.

Experimental. Red crystal approximately 0·43 × 0·51 × 0·58 mm, from methanol solution, Siemens AED single-crystal diffractometer with an IBM PS/2 M30 computer, Cu $K\alpha$ radiation, cell parameters from least-squares treatment of setting angles of 21 reflections $(19 \le \theta \le 44°)$, one standard reflection monitored every 50 counts showed no more than 0·3%