forms two hydrogen bonds to the oxime O atoms of adjacent $[(NH_3)_2Co(Hdmg)_2]^+$ cations [N(3)–H(2)$\cdots$O(2) at x, $1 + y$, z, N$\cdots$O = 2·94 Å, and N(3)–H(3)$\cdots$O(1) at x, $\frac{1}{2} - y$, $-\frac{1}{2} + z$, N$\cdots$O = 3·02 Å] and only one comparable bond to the NO_3^- anion [N(3)–H(1)$\cdots$O(3) at $1 - x$, $\bar{y}$, $\bar{z}$, N$\cdots$O = 2·96 Å] may give some indication why the nitrate is not ordered in this structure.

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References

Bresciani-Pahor, N., Calligaris, M. & Randaccio, L. (1978). *Inorg. Chim. Acta*, **27**, 47–52.

Heeg, M. J. & Elder, R. C. (1980). *Inorg. Chem.* **19**, 932–934.

Heeg, M. J., Elder, R. C. & Deutsch, E. (1980). *Inorg. Chem.* **19**, 554–556.

Nakatsuka, Y. & Iinuma, H. (1936). *Bull. Chem. Soc. Jpn*, **11**, 48–54.

Palenik, G. J., Sullivan, D. A. & Naik, D. V. (1976). *J. Am. Chem. Soc.* **98**, 1177–1182.

Viswanathan, K. S. & Kunchur, N. R. (1961). *Acta Cryst.* **14**, 675–679.

Acta Cryst. (1980). B**36**, 2431–2433

Sodium 5,6-Dihydrouracil-6-sulfonate Monohydrate

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Abstract. $C_4H_5N_2O_5S^-.Na^+.H_2O$, $P2_1/c$, a = 5·668 (1), b = 11·026 (2), c = 13·261 (2) Å, β = 94·62 (2)°, Z = 4, D_c = 1·884, D_o = 1·87 Mg m^{-3}, V = 826·1 Å^3, M_r = 234·1, λ(Mo $K\alpha$) = 0·71069 Å, T = 299 ± 1 K, $F(000)$ = 480. The intensity data were collected on an automated diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement, with the temperature factors of the non-hydrogen atoms allowed to refine anisotropically, yielded an R of 0·032 for the 1735 significant data. The modified pyrimidine anions are packed as hydrogen-bonded, centrosymmetrically related pairs, bridged by coordination bonds to the Na^+ ion and hydrogen bonds with the water molecule.

Introduction. The title compound was obtained as a by-product of the synthesis of N^4-semicarbazido-5,6-dihydrocytosine 6-sulfonate. Nitrogen nucleophiles, such as semicarbazide and bisulfite, are mutagenic, and are believed to induce mutations by reaction with cytosine residues in polynucleotides (Hayatsu, 1976*a*; Budowsky, 1976). Recently, Hayatsu has reported a 'cooperative' action in the induction of mutations by combinations of bisulfite and several nitrogen nucleophiles, including semicarbazide (Hayatsu, 1977). As the mechanism of mutation is in question, structure determinations of reaction products of these mutagens with cytosine can be important.

N^4-Semicarbazido-5,6-dihydrocytosine 6-sulfonate was synthesized according to Hayatsu (1976*b*). The identity of the resulting finely divided powder was confirmed by spectral analysis: UV, in water, λ_{max} 243 nm, λ_{min} 214 nm; in 0·1 M NaOH, λ_{max} 265 nm, λ_{min} 227 nm. Attempts to recrystallize the material from 0·2 M $NaHSO_3$–Na_2SO_3, pH 7, as suggested by Hayatsu, resulted, in our hands, in well formed crystals of 5,6-dihydrouracil-6-sulfonate. Recrystallization from water and from neutral solutions of semicarbazide also gave the elimination product. The identity of the crystalline material was established by its UV spectrum in water and by its reversal to uracil upon treatment with alkali (Hayatsu, 1976*b*).

As the apparent lability of the semicarbazide group suggests a significant role for the deaminated product in the mutagenic activity of semicarbazide–bisulfite reactions with cytosine, a structure determination of 5,6-dihydrouracil-6-sulfonate was undertaken.

A crystal 0·30 × 0·35 × 0·30 mm was selected for diffraction study. The space group and approximate cell dimensions were determined from precession and Weissenberg photographs. More-accurate cell dimensions were obtained by least-squares refinement of the first moments of 40 observed 2θ values in the range $45 < 2\theta < 53°$ [r.m.s. $(\theta_c - \theta_o)$ = 0·026°], measured with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). The density of the crystals was determined by flotation in mixtures of chloroform and

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Table 1. *Positional and isotropic thermal parameters* (×10⁴) *for non-hydrogen atoms*

The isotropic temperature factor is $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$; the values given are the arithmetic averages of the principal components of the anisotropic temperature factors. Standard deviations in units of the last significant digits are in parentheses.

	x	y	z	U (Å^2)
N(1)	634 (3)	3374 (1)	−38 (1)	257 (7)
C(2)	2420 (3)	3868 (2)	−496 (1)	220 (7)
O(2)	2520 (3)	4958 (1)	−712 (1)	292 (7)
N(3)	4223 (3)	3104 (1)	−753 (1)	254 (7)
C(4)	4202 (3)	1864 (2)	−683 (1)	226 (8)
O(4)	5827 (3)	1267 (1)	−980 (1)	324 (7)
C(5)	2069 (3)	1301 (2)	−275 (1)	255 (8)
C(6)	650 (3)	2148 (2)	353 (1)	214 (7)
S	1718 (1)	2146 (1)	1678 (1)	191 (2)
O(11)	4217 (2)	2484 (1)	1714 (1)	282 (7)
O(12)	1354 (2)	904 (1)	2016 (1)	271 (6)
O(13)	267 (3)	3032 (1)	2157 (1)	328 (7)
Na	6589 (1)	836 (1)	−2712 (1)	251 (3)
O(w)	3222 (3)	−525 (2)	−2842 (2)	446 (9)

dibromomethane. Intensity data were collected on the diffractometer with Nb-filtered Mo $K\bar{\alpha}$ radiation using the θ–2θ scan technique. Of 1916 reflections with $2\theta < 55°$, 1735 were considered observed $[|F_o| > 3\sigma(F_o)]$. Each intensity was assigned a variance $\sigma^2(I)$ based on counting statistics plus a term $(0{\cdot}04I)^2$ empirically derived during refinement. No absorption correction was applied ($\mu = 0{\cdot}45$ mm^{-1}). No significant changes were observed in two standard reflections during the course of the data collection.

The structure was solved with the aid of the direct-methods computer program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and the H atoms were located from a difference electron density map. The atomic parameters were refined by full-matrix least-squares methods. The non-hydrogen atoms were refined with anisotropic thermal parameters and the H atoms with isotropic thermal parameters. The final values of R, the weighted R $\{[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}\}$, and σ, the goodness of fit $\{[\sum w(F_o - F_c)^2/(n-p)]^{1/2}$, where n = 1735 reflections and p = 155 variables$\}$, were 0·032, 0·042 and 1·54, respectively. All refinements were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The final atomic parameters are given in Table 1.*

Discussion. A drawing of the anion, including bond distances and angles, is shown in Fig. 1. The bond distances and angles in the six-membered ring are consistent with those observed in other dihydro-diketo pyrimidines [dihydrouracil (Rohrer & Sundaralingam, 1970); dihydrouridine (Sundaralingam, Rao & Abola, 1971); 5,6-dihydro-2-thiouracil (Kojić-Prodić, Ružić-Toroš & Coffou, 1976); 5,6-dihydro-2-thiouracil-6-sulfonate (Jain, Lee, Mertes & Pitman, 1978)]. As in 5,6-dihydro-2-thiouracil-6-sulfonate, the sulfonate group is attached *axially* to the puckered ring. The C—S and S—O bond distances reported for 5,6-dihydro-2-thiouracil-6-sulfonate are 1·818 (2) and 1·461 (2), 1·464 (2) and 1·447 (2) Å. In both structures, the sulfonate O atoms are nearly staggered with respect to the substituents on C(6).

That the six-membered ring is significantly puckered is reflected in the torsion angles given in Table 2. The best four-atom least-squares plane is through atoms C(2), N(3), C(4) and C(5). The r.m.s. deviation of these atoms from the plane is 0·007 Å. N(1) and C(6) are displaced on the same side of this plane by 0·206 and 0·763 Å, compared to 0·197 and 0·729 and 0·133 and 0·759 Å for the two independent molecules of dihydrouridine (Sundaralingam *et al.*, 1971). The ring pucker is significantly different from that observed in 5,6-dihydro-2-thiouracil-6-sulfonate (Jain *et al.*, 1978).

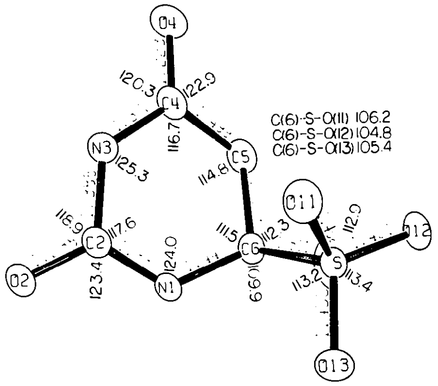

Fig. 1. Bond distances (Å) and angles (°). The boundary thermal ellipsoids are drawn at the 50% probability level. The average standard deviations in the bond lengths and angles are 0·002 Å and 0·2°, respectively. Illustrations were prepared with the aid of the computer program *ORTEP* (Johnson, 1965).

Table 2. *Torsion angles* (°)

The positive sense of rotation is clockwise while looking along the *BC* bond.

A–B–C–D	
C(6)–N(1)–C(2)–N(3)	10·6 (2)
N(1)–C(2)–N(3)–C(4)	7·9 (2)
C(2)–N(3)–C(4)–C(5)	−1·3 (2)
N(3)–C(4)–C(5)–C(6)	−21·2 (2)
C(4)–C(5)–C(6)–N(1)	35·5 (2)
C(5)–C(6)–N(1)–C(2)	−31·9 (2)

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* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35378 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

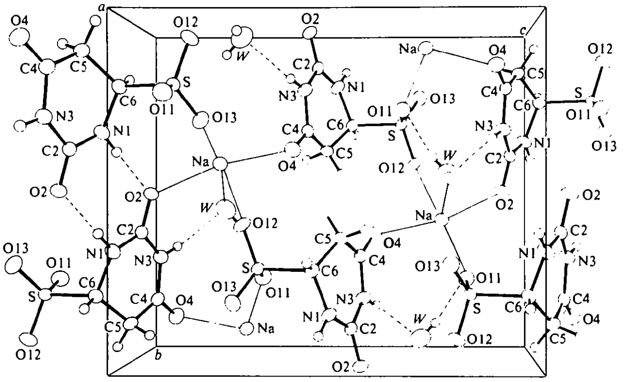

Fig. 2. Packing interactions. The dashed lines represent hydrogen bonds. The fine solid lines represent the Na$^+$ ion coordination. One hydrogen bond, O(w)–H(w,2)$\cdots$O(12), was left out for clarity.

Table 3. *Hydrogen-bond parameters*

X–H$\cdots Y$	$X\cdots Y$ (Å)	H$\cdots Y$ (Å)	X–H$\cdots Y$ (°)
N(1)–H(1)$\cdots$O(2)$^{\rm i}$	2·803 (2)	1·96 (3)	177 (3)
N(3)–H(3)$\cdots$O(w)$^{\rm ii}$	2·880 (3)	2·12 (3)	155 (3)
O(w)–H(w,1)$\cdots$O(11)$^{\rm iii}$	2·943 (2)	2·28 (7)	149 (6)
O(w)–H(w,2)$\cdots$O(12)$^{\rm iv}$	2·925 (2)	2·26 (4)	147 (4)

Symmetry code for superscripts

(i) $-x, 1-y, -z$
(ii) $1-x, \frac{1}{2}+y, -\frac{1}{2}-z$
(iii) $1-x, -y, -z$
(iv) $-x,-y,-z$

The r.m.s. deviation of atoms N(1), C(2), N(3) and C(4) from their least-squares plane is 0·042 Å in the present structure and 0·021 Å in 5,6-dihydro-2-thiouracil-6-sulfonate. Atoms C(5) and C(6) are displaced to opposite sides of this plane by 0·167 and 0·486 Å in the present structure, and 0·323 and 0·198 Å in 5,6-dihydro-2-thiouracil-6-sulfonate.

Fig. 2 is a view of the packing interactions. The hydrogen bonds and Na$^+$ ion coordination are given in Tables 3 and 4. The anions are packed as hydrogen-bonded pairs related by a center of symmetry. The Na$^+$ ion coordination and hydrogen bonds to the water molecule bridge adjacent pairs.

Table 4. *Sodium ion coordination*

Na–O(2)$^{\rm i}$	2·394 (2) Å	Na–O(12)$^{\rm iii}$	2·391 (2) Å
Na–O(4)	2·418 (2)	Na–O(13)$^{\rm iv}$	2·448 (2)
Na–O(11)$^{\rm ii}$	2·378 (2)	Na–O(w)	2·423 (2)

Symmetry code for superscripts

(i) $1-x, -\frac{1}{2}+y, -\frac{1}{2}-z$
(ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$
(iii) $1-x, -y, -z$
(iv) $1+x, \frac{1}{2}-y, -\frac{1}{2}+z$

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References

Budowsky, E. I. (1976). *Prog. Nucleic Acid Res. Mol. Biol.* **16**, 125–188.

Busing, W. R., Ellison, R. D., Levy, H. A., King, S. P. & Roseberry, R. T. (1968). Report ORNL-4143. Oak Ridge National Laboratory, Tennessee.

Hayatsu, H. (1976*a*). *Prog. Nucleic Acid Res. Mol. Biol.* **16**, 75–124.

Hayatsu, H. (1976*b*). *Biochemistry*, **15**, 2677–2682.

Hayatsu, H. (1977). *J. Mol. Biol.* **115**, 19–31.

Jain, N. B., Lee, B., Mertes, K. B. & Pitman, I. H. (1978). *Acta Cryst.* B**34**, 927–930.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kojić-Prodić, B., Ružić-Toroš, Z. & Coffou, E. (1976). *Acta Cryst.* B**32**, 1099–1102.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-La-Neuve, Belgium.

Rohrer, D. C. & Sundaralingam, M. (1970). *Acta Cryst.* B**26**, 546–553.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Sundaralingam, M., Rao, S. T. & Abola, J. (1971). *J. Am. Chem. Soc.* **93**, 7055–7062.