greater than the average values 1·421 (9) and 1·252 (7) Å reported earlier.

The perchlorate ions completing the structure show some of the expected disorder and the variations in the observed Cl–O bond lengths are rather large, 1·34–1·43 Å (Table 3). The O–Cl–O angles range from 104 to 112°. Two of the O atoms in each of the perchlorate groups are apparently involved in hydrogen-bond formation to the amine N atoms. The most probable hydrogen-bonding scheme is one consisting of four relatively weak interactions [3·217 (7)–3·252 (12) Å] between the O atoms of one perchlorate and the two nearest complex cations, and three, somewhat stronger bonds [3·017 (10), 3·021 (10) and 3·263 (9) Å] between the O atoms of the other perchlorate and a total of three different cations. The hydrogen-bond contacts in the structure are not only associated with the perchlorate groups: the closest interionic contact [2·944 (6) Å] involves the oxime O atom, which accepts a hydrogen bond from the amine N atom in an adjacent complex cation. In this way all eight amino H atoms are active in hydrogen bonding. Details of the proposed hydrogen-bond network are presented in Table 4.

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

X–H···Y	Position of Y	X···Y	X–H···Y
N(2)–H1(N2)···O(7)	$x, 1-y, z$	3·021 (10)	165 (6)
N(2)–H2(N2)···O(3)	$-1-x, -\frac{1}{2}+y, \frac{1}{2}-z$	3·212 (7)	166 (5)
N(3)–H1(N3)···O(8)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	3·263 (9)	138 (8)
N(3)–H2(N3)···O(5)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	3·252 (12)	124 (6)
N(4)–H1(N4)···O(8)	x,y,z	3·017 (10)	157 (5)
N(4)–H2(N4)···O(2)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	2·944 (6)	154 (6)
N(5)–H1(N5)···O(3)	$-1-x, -\frac{1}{2}+y, \frac{1}{2}-z$	3·217 (7)	139 (7)
N(5)–H2(N5)···O(5)	$-1-x, -\frac{1}{2}+y, \frac{1}{2}-z$	3·227 (10)	151 (5)

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The Structure of the Complex Dicytosinium Tetrachlorocuprate

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Abstract. $[C_4H_6N_3O]_2[CuCl_4]$, triclinic, $P\bar{1}$, a = 13·689 (2), b = 9·537 (1), c = 6·936 (1) Å, α = 102·93 (2), β = 105·59 (2), γ = 112·24 (2)°, Z = 2, D_m = 1·875 (3) Mg m^{-3}. The final R value is 0·082 for 2711 non-zero reflections observed on a diffractometer. There is no direct coordination between the metal atoms and cytosinium cations. The base pairing related by a center of symmetry is formed by two N(1)–H···O(2) hydrogen bonds (2·85 Å). The main intermolecular interactions consist of five kinds of N–H··· Cl hydrogen bonds.

Introduction. Brownish crystals were prepared by slow evaporation of a 0·1 *M* HCl solution (50 ml) containing 220 mg of cytosine and 5 g of $CuCl_2.2H_2O$ which had been heated at 243 K for several hours.

Three-dimensional intensity data were collected with a crystal 0·25 × 0·25 × 0·58 mm on a Rigaku computer-controlled four-circle diffractometer using monochromated Mo $K\alpha$ radiation. With the ω–2θ scan technique, a scan speed of 4° (2θ) min^{-1} and 10 s background measurements at each end of the scan, 2711 independent non-zero reflections were obtained with $\sin\theta/\lambda < 0{\cdot}65$ Å^{-1}.

The structure was solved by the heavy-atom method, and refined by a block-diagonal least-squares procedure

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with anisotropic temperature factors for all non-hydrogen atoms. The H atom coordinates were geometrically assumed and were included in the further refinement. The function $\sum w(|F_o| - |F_c|)^2$, with weights w, was minimized. The scattering factors used were those cited in *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1, and bond distances and angles are listed in Table 2.*

Discussion. There is no direct coordination between the Cu atom and the cytosinium ions. The bond distances in two independent cytosinium ions [CytH$^+$ (I) and CytH$^+$ (II)] are similar to those found in [cytosine.H]$_2^+$.[PdCl$_4$]$^{2-}$ (Kindberg & Amma, 1975). The bond angles of C(2)—N(3)—C(4) in both cytosinium ions are larger than that of unprotonated cytosine as suggested by Singh (1965). The difference Fourier map clearly showed all H atoms including those attached at both N(3) atoms.

The two pyrimidinium rings are almost planar with maximum deviations of 0·0035 Å at C(4) of CytH$^+$ (I) and 0·0191 Å at N(3) of CytH$^+$ (II) (Table 3).

As shown in Table 2, the geometry of the tetrachlorocuprate anion is a distorted-tetrahedral coordination as found in the crystal structures of [(C$_2$H$_5$)$_3$-

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34203 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates with their estimated standard deviations in parentheses*

	x	y	z
[CuCl$_4$]$^{2-}$			
Cu	0·2313 (1)	0·0737 (1)	0·2184 (2)
Cl(1)	0·3425 (2)	0·3455 (2)	0·3974 (4)
Cl(2)	0·1229 (2)	0·0919 (3)	−0·0728 (3)
Cl(3)	0·2189 (2)	0·0138 (3)	0·5019 (4)
Cl(4)	0·2470 (2)	−0·1404 (2)	0·0477 (4)
Cytosinium$^+$ (I)			
N(1)	0·1578 (6)	0·6014 (8)	0·2949 (12)
C(2)	0·0951 (8)	0·4458 (10)	0·1468 (13)
O(2)	0·0763 (7)	0·4129 (8)	−0·0420 (10)
N(3)	0·0543 (6)	0·3290 (8)	0·2340 (10)
C(4)	0·0717 (7)	0·3586 (8)	0·4441 (11)
N(4)	0·0268 (7)	0·2371 (8)	0·5032 (12)
C(5)	0·1378 (7)	0·5218 (9)	0·5881 (12)
C(6)	0·1785 (7)	0·6386 (9)	0·5091 (12)
HN(1)	0·18 (1)	0·68 (1)	0·25 (1)
HN(3)	0·01 (1)	0·21 (1)	0·10 (2)
HN(4)	−0·02 (1)	0·13 (1)	0·42 (2)
HN(4)	0·04 (1)	0·27 (1)	0·65 (2)
HC(5)	0·14 (1)	0·54 (1)	0·74 (2)
HC(6)	0·22 (1)	0·76 (1)	0·59 (2)
Cytosinium$^+$ (II)			
N(1)	0·5034 (7)	0·8729 (8)	0·2617 (12)
C(2)	0·4398 (8)	0·7650 (9)	0·3242 (14)
O(2)	0·4313 (6)	0·8023 (8)	0·4950 (10)
N(3)	0·3842 (6)	0·6048 (8)	0·1833 (11)
C(4)	0·3849 (7)	0·5547 (10)	−0·0165 (13)
N(4)	0·3240 (7)	0·3989 (8)	−0·1326 (12)
C(5)	0·4508 (8)	0·6727 (7)	−0·0830 (15)
C(6)	0·5103 (8)	0·8283 (11)	0·0556 (17)
HN(1)	0·53 (1)	0·99 (1)	0·37 (2)
HN(3)	0·34 (1)	0·52 (1)	0·26 (2)
HN(4)	0·27 (1)	0·31 (1)	−0·10 (2)
HN(4)	0·32 (1)	0·36 (1)	−0·26 (2)
HC(5)	0·46 (1)	0·65 (1)	−0·24 (2)
HC(6)	0·57 (1)	0·92 (1)	0·03 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *with their estimated standard deviations in parentheses*

CuCl$_4^{2-}$		CuCl$_4^{2-}$	
Cu—Cl(1)	2·266 (3)	Cl(1)—Cu—Cl(2)	95·8 (1)
Cu—Cl(2)	2·248 (3)	Cl(1)—Cu—Cl(3)	96·1 (1)
Cu—Cl(3)	2·198 (3)	Cl(1)—Cu—Cl(4)	138·6 (1)
Cu—Cl(4)	2·236 (3)	Cl(2)—Cu—Cl(3)	139·8 (1)
		Cl(2)—Cu—Cl(4)	97·9 (1)
		Cl(3)—Cu—Cl(4)	98·2 (1)

	CytH$^+$ (I)	CytH$^+$ (II)
N(1)—C(2)	1·37 (1)	1·36 (1)
C(2)—O(2)	1·21 (1)	1·21 (1)
C(2)—N(3)	1·39 (1)	1·39 (1)
N(3)—C(4)	1·36 (1)	1·37 (1)
C(4)—N(4)	1·30 (1)	1·31 (1)
C(4)—C(5)	1·41 (1)	1·41 (2)
C(5)—C(6)	1·36 (1)	1·35 (2)
N(1)—C(6)	1·37 (1)	1·37 (2)

	CytH$^+$ (I)	CytH$^+$ (II)
C(2)—N(1)—C(6)	123·2 (9)	123·4 (9)
N(1)—C(2)—O(2)	123·3 (10)	124·3 (10)
N(1)—C(2)—N(3)	113·7 (9)	113·9 (9)
O(2)—C(2)—N(3)	123·0 (10)	121·8 (10)
C(2)—N(3)—C(4)	125·7 (8)	125·0 (9)
N(3)—C(4)—N(4)	119·2 (9)	117·1 (9)
N(3)—C(4)—C(5)	117·6 (8)	118·2 (9)
N(4)—C(4)—C(5)	123·3 (9)	124·7 (10)
C(4)—C(5)—C(6)	118·4 (9)	117·9 (10)
N(1)—C(6)—C(5)	121·5 (9)	121·6 (11)

Table 3. *Deviations* (Å) *of atoms from the least-squares planes of the two pyrimidinium rings*

The equations of the planes are $0{\cdot}9734X - 0{\cdot}1660Y + 0{\cdot}1551Z + 1{\cdot}0162 = 0{\cdot}0$ and $-0{\cdot}8653X + 0{\cdot}2986Y - 0{\cdot}4026Z - 1{\cdot}3449 = 0{\cdot}0$ for CytH$^+$ (I) and CytH$^+$ (II), respectively, where $X = ax + by\cos\gamma + cz\cos\beta$, $Y = by\sin\gamma - cz\cos\alpha^*\sin\beta$ and $Z = cz\sin\alpha^*\sin\beta^*$ (x, y and z are fractional coordinates). Asterisks indicate the atoms which are included in the calculation of the least-squares planes.

	CytH$^+$ (I)	CytH$^+$ (II)
N(1)*	−0·001 (9)	0·002 (9)
C(2)*	0·001 (10)	0·016 (10)
O(2)	−0·006 (9)	0·054 (8)
N(3)*	0·002 (8)	−0·019 (9)
C(4)*	−0·004 (9)	0·007 (10)
N(4)	−0·022 (10)	0·020 (10)
C(5)*	0·003 (10)	0·014 (11)
C(6)*	−0·001 (10)	−0·019 (12)

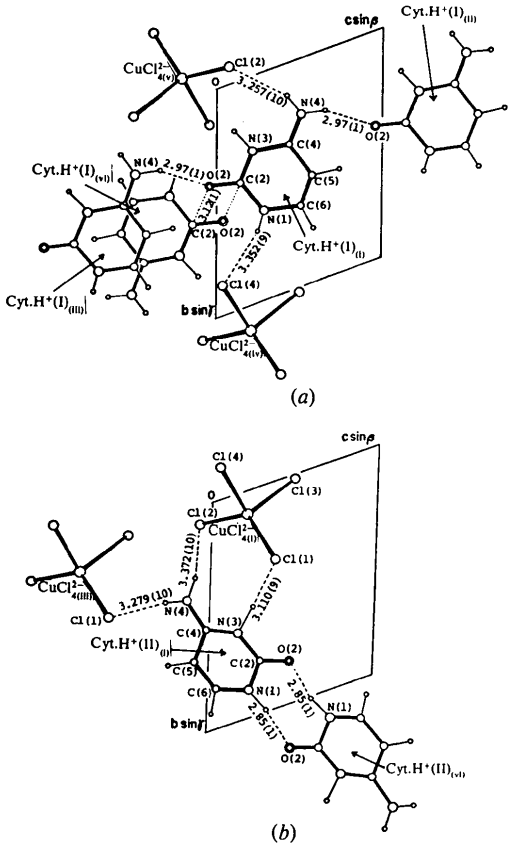

Fig. 1. The molecular packing projected along the *a* axis. (*a*) Interactions involving CytH$^+$ (I), (*b*) interactions involving CytH$^+$ (II), where the broken lines and dotted lines indicate the hydrogen bonds and the dipole–dipole short contacts, respectively. Symmetry code: (i) x,y,z; (ii) $x, y, 1+z$; (iii) $x, y, -1+z$; (iv) $x, -1+y, z$; (v) $-x,-y,-z$; (vi) $-x, 1-y, -z$; (vii) $1-x, 2-y, 1-z$.

NH]$_2$.CuCl$_4$ (Lamotte-Brasseur, Dupont & Dideberg, 1973) and thiamine hydrochloride Cu^{II} complex (Caira, Fazakerley, Linder & Nassimbeni, 1974).

The molecular packing is shown in Figs. 1 and 2. It is of interest to note that the base pairing is formed only between two CytH$^+$ (II) cations related by a center of symmetry and two N(1)—H···O(2) hydrogen bonds (distance 2·85 Å). Such a base pair is frequently observed in cytosine derivatives including the cytosine–cytosinium–$\frac{1}{2}$[ZnCl$_4$]$^{2-}$ complex (Fujinami, Ogawa, Arakawa, Fujii, Shirotake & Tomita, 1979). However, there are two kinds of intermolecular interactions between two CytH$^+$ (I) molecules: a dipole–dipole interaction with a short contact of 3·12 Å [C(2)···O(2)] between carbonyl groups related by a center of symmetry, and a hydrogen bond of length 2·97 Å between the N(4) atom and the adjacent O(2) atom translated by one unit along the *c* axis.

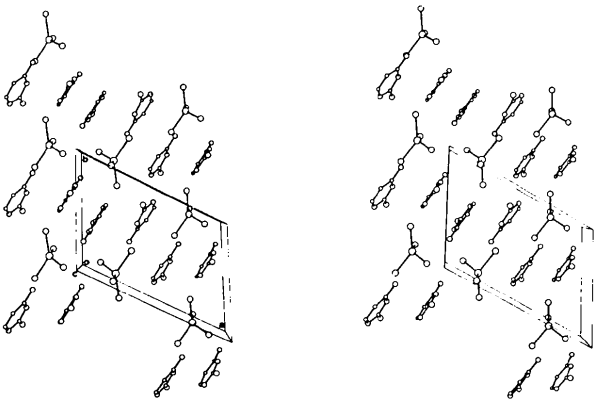

Fig. 2. A stereoscopic illustration of the molecular packing viewed along the *c* axis.

Between the tetrachlorocuprate anion and cytosinium cations there are five kinds of N—H···Cl hydrogen bonds as shown in Fig. 1(*a*) and (*b*), an interaction being considered as a possible N—H···Cl hydrogen bond when the interatomic distance between a Cl and a H atom is less than 2·6 Å (Hamilton & Ibers, 1968). Out of the four Cl atoms, three participate in hydrogen bonds, and the remaining Cl(3) atom has a significantly shorter Cu—Cl distance (2·198 Å) than the others.

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