

The Structure of the Complex Cytosinium Hemitetrachlorozincate–Cytosine

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(Received 6 November 1978; accepted 18 January 1979)

Abstract. $[\text{C}_4\text{H}_6\text{N}_3\text{O}]_2^+[\text{ZnCl}_4]^{2-} \cdot \text{C}_4\text{H}_5\text{N}_3\text{O}$, monoclinic, $C2/c$, $a = 7.054$ (1), $b = 15.182$ (1), $c = 23.756$ (3) Å, $\beta = 94.67$ (1)°, $Z = 8$. The structure was refined to give $R = 0.075$ for 1893 independent reflections. No direct coordination between the Zn atom and Cyt or CytH⁺ molecules is observed. Two kinds of base pairing are formed alternately between Cyt and CytH⁺. Infinite hydrogen-bonded pyrimidine–pyrimidinium elongated ribbon-like sheets stack along the b axis with a separation of 3.26 Å. The distorted-tetrahedral $[\text{ZnCl}_4]^{2-}$ ion is fixed between the parallel sheets by N–H...Cl and C–H...Cl hydrogen bonds.

Introduction. The unit-cell dimensions were obtained from a least-squares fitting procedure on the θ values of 11 reflections ($0.14 \leq \sin \theta/\lambda \leq 0.33$ Å⁻¹) observed with Cu $K\alpha$ radiation and the ω – 2θ scan technique. A pillar-shaped crystal with dimensions ca 0.50 × 0.20 × 0.07 mm was used and 1942 reflections within $\sin \theta/\lambda = 0.58$ Å⁻¹ were measured, of which 1893 having intensities greater than 2.5 times their standard deviations were used for the analysis. Usual corrections for Lorentz and polarization factors were made but not for absorption because of the small size of the crystal. The structure was solved by Patterson and Fourier methods and refined by a block-diagonal least-squares procedure. All the H atoms could be located in a difference Fourier map. The final R value is 0.075 for all reflections.

Discussion. As confirmed by a difference Fourier map, the two cytosine molecules in each asymmetric unit are a cytosine ion (CytH⁺) and a neutral cytosine (Cyt). The Zn atom of $[\text{ZnCl}_4]^{2-}$ lies on a twofold axis. No direct interaction between the metal and the pyrimidine base was found. The final fractional coordinates are listed in Table 1.

Table 2 shows the bond lengths and angles in CytH⁺ and Cyt, which agree well with those found in other related molecules (Kindberg & Amma, 1975; Jeffrey &

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

	x	y	z
$[\text{ZnCl}_4]^{2-}$			
Zn	1.0000 (0)*	0.08402 (4)	0.2500 (0)*
Cl(1)	0.8355 (2)	0.0084 (1)	0.1808 (1)
Cl(2)	1.2136 (2)	0.1699 (1)	0.2082 (1)
Cytosinium ⁺			
N(1)	0.8123 (5)	0.4768 (2)	0.1203 (1)
C(2)	0.7219 (6)	0.4235 (2)	0.0802 (2)
O(2)	0.6939 (5)	0.4449 (2)	0.0304 (1)
N(3)	0.6644 (5)	0.3433 (2)	0.0977 (1)
C(4)	0.6939 (6)	0.3128 (2)	0.1515 (2)
N(4)	0.6383 (6)	0.2347 (2)	0.1631 (1)
C(5)	0.7851 (6)	0.3719 (3)	0.1929 (2)
C(6)	0.8405 (6)	0.4495 (3)	0.1755 (2)
HN(1)	0.862 (9)	0.534 (4)	0.108 (2)
HN(3)	0.615 (9)	0.309 (4)	0.067 (2)
HN(4)	0.582 (9)	0.202 (4)	0.134 (3)
HN(4)	0.657 (9)	0.208 (4)	0.193 (2)
HC(5)	0.808 (9)	0.345 (3)	0.228 (3)
HC(6)	0.909 (8)	0.488 (3)	0.205 (2)
Cytosine			
N(1)	1.1563 (5)	0.3999 (2)	0.0116 (2)
C(2)	1.0611 (6)	0.3440 (2)	–0.0261 (2)
O(2)	1.0351 (5)	0.3680 (2)	–0.0766 (1)
N(3)	0.9977 (5)	0.2655 (2)	–0.0079 (1)
C(4)	1.0309 (5)	0.2445 (2)	0.0470 (2)
N(4)	0.9663 (6)	0.1667 (2)	0.0637 (2)
C(5)	1.1281 (6)	0.3018 (3)	0.0870 (2)
C(6)	1.1881 (6)	0.3790 (3)	0.0671 (2)
HN(1)	1.197 (9)	0.457 (4)	–0.006 (3)
HN(4)	0.890 (8)	0.126 (4)	0.033 (2)
HN(4)	0.997 (9)	0.140 (4)	0.102 (2)
HC(5)	1.144 (9)	0.291 (4)	0.123 (2)
HC(6)	1.270 (9)	0.422 (3)	0.096 (3)

* Fixed by symmetry.

Kinoshita, 1963).† It is worth noting that the variety in the Zn–Cl distances [2.248 (2) and 2.280 (1) Å] and Cl–Zn–Cl angles [106.86 (5), 110.27 (5), 117.30 (5), and 118.61 (6)°] may be partly due to the

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34204 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

[ZnCl ₄] ²⁻		[ZnCl ₄] ²⁻	
Zn—Cl(1)	2.248 (2)	Cl(1)—Zn—Cl(1')	118.61 (6)
Zn—Cl(2)	2.280 (1)	Cl(1)—Zn—Cl(2)	106.86 (5)
		Cl(1)—Zn—Cl(2')	117.30 (5)
		Cl(2)—Zn—Cl(2')	110.27 (5)
		Cytosinium	Cytosine
N(1)—C(2)	1.368 (6)	1.368 (5)	
C(2)—O(2)	1.230 (6)	1.254 (5)	
C(2)—N(3)	1.359 (5)	1.355 (5)	
N(3)—C(4)	1.360 (5)	1.344 (5)	
C(4)—N(4)	1.285 (6)	1.337 (6)	
C(4)—C(5)	1.444 (6)	1.426 (6)	
C(5)—C(6)	1.319 (6)	1.344 (6)	
N(1)—C(6)	1.374 (6)	1.359 (6)	
		Cytosinium	Cytosine
C(2)—N(1)—C(6)	120.7 (4)	121.5 (4)	
N(1)—C(2)—O(2)	123.0 (4)	118.0 (4)	
N(1)—C(2)—N(3)	116.9 (4)	119.7 (4)	
O(2)—C(2)—N(3)	120.2 (4)	122.3 (3)	
C(2)—N(3)—C(4)	124.4 (4)	118.8 (3)	
N(3)—C(4)—N(4)	119.3 (4)	117.4 (4)	
N(3)—C(4)—C(5)	117.1 (4)	122.7 (4)	
N(4)—C(4)—C(5)	123.6 (4)	119.9 (4)	
C(4)—C(5)—C(6)	118.0 (4)	116.4 (4)	
N(1)—C(6)—C(5)	123.0 (4)	121.0 (4)	

intermolecular hydrogen bond between the Cl atoms and the neighboring CytH⁺ or Cyt.

The cytosine ring including the exocyclic N(4) and O(2) atoms is approximately planar with a maximum deviation from the least-squares plane of less than 0.01 Å, but the N(4) and C(4) atoms of CytH⁺ deviate slightly probably because of hydrogen-bond formation with the Cl atom (Table 3).

Fig. 1(a) indicates two independent hydrogen-bonded base pairings between CytH⁺ and Cyt molecules, both of which occur between two molecules related by pseudosymmetry, that is, CytH⁺ (i) and Cyt (ii), and CytH⁺ (i) and Cyt (iii). The latter 'symmetric' or 'self'-hydrogen-bonded pairing mode is found commonly in the crystal structures of cytosine and uracil derivatives (Voet & Rich, 1969; Reeke & Marsh, 1966). The protonation at N(3) allows an unusual triply hydrogen-bonded pair to form in a similar manner as has been found in the crystal structures of cytosine-resorcylic acid 2:1 complex (Tamura, Sato & Hata, 1973), cytosine-5-acetic acid (Marsh, Bienstadt & Eichhorn, 1962) and the double-stranded polycytidylic acid at pH 5.5 or less (Langridge & Rich, 1963).

The base stacking is shown in Fig. 1(b) and the alternate triply and doubly hydrogen-bonded base pairings form an infinite sheet elongated along the *b* axis. There are two stacking modes between the base-pairing sheets. The overlap (I) between the upper and middle base pairings is greater than the overlap (II) between the middle and the lower ones. The average stacking distances, however, are nearly equal in both

cases (3.26 Å), which indicates the strong stacking interaction.

According to the criterion of Hamilton & Ibers (1968), Cl atoms are involved in hydrogen bonds with either the amino N(4) of CytH⁺ or the ring C(6) atom of Cyt, and these interactions may be responsible for

Table 3. Deviations (Å) of each atom from the least-squares planes of the pyrimidine or pyrimidinium rings

The equations of the planes are $-0.8862X + 0.4243Y + 0.1859Z + 4.5785 = 0.0$ and $0.9022X - 0.3859Y - 0.1927Z + 1.1046 = 0.0$ for cytosine and cytosinium, respectively. Asterisks indicate the atoms which are included in the calculation of the least-squares planes.

	Cytosine	Cytosinium
N(1)*	-0.004 (4)	-0.007 (4)
C(2)*	0.001 (4)	0.004 (4)
O(2)	0.009 (3)	-0.008 (4)
N(3)*	0.003 (3)	0.009 (3)
C(4)*	-0.004 (4)	-0.017 (4)
N(4)	0.000 (4)	-0.047 (4)
C(5)*	0.002 (4)	0.010 (4)
C(6)*	0.002 (4)	0.002 (4)

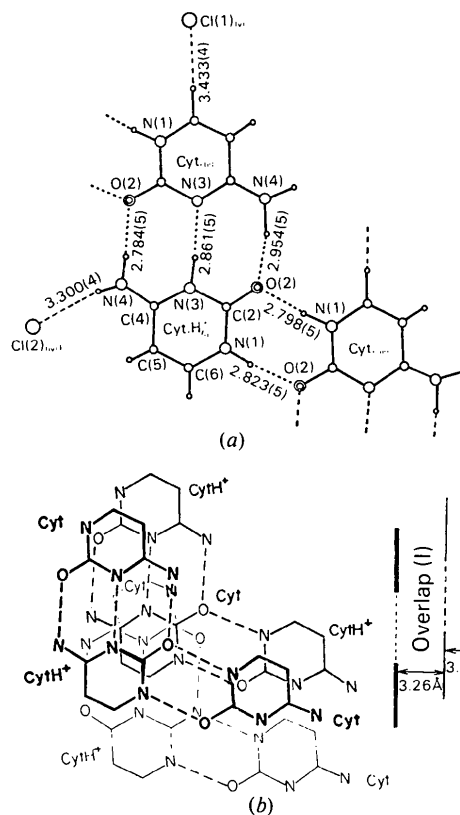


Fig. 1. (a) The hydrogen-bonded base pairings and (b) the overlapping of bases. Dashed lines indicate hydrogen bonds and small open circles represent H atoms. Symmetry code: (i) x, y, z ; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $2 - x, 1 - y, -z$; (iv) $2 - x, y, \frac{1}{2} - z$; (v) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$.

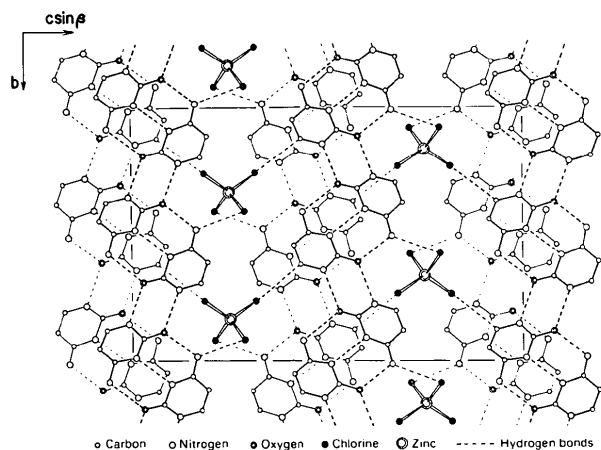


Fig. 2. The *a* axis projection of the crystal structure. The dashed lines indicate hydrogen bonds.

Acta Cryst. (1979). **B35**, 970–973

(+)-Lupanine Perchlorate Monohydrate

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(Received 6 July 1978; accepted 6 November 1978)

Abstract. $C_{15}H_{25}N_2O^+ \cdot ClO_4^- \cdot H_2O$, monoclinic, $M_r = 366.9$, $P2_1$, $Z = 2$, $a = 9.014$ (2), $b = 15.491$ (2), $c = 7.473$ (1) Å, $\beta = 123.32$ (1)°, $\mu(Cu K\alpha) = 2.25$ mm⁻¹, $D_c = 1.40$ Mg m⁻³; $R = 0.044$, $R_w = 0.049$ for 835 reflections. The *C* ring of the lupanine skeleton adopts the boat conformation. The lupanine cations are linked together by a hydrogen-bond network utilizing the O atom from the water molecule [N(16)···O(W)···O(C2): N(16)···O(W) = 2.817 Å, O(W)···O(C2) = 2.717 Å].

Introduction. This work is an extension of the X-ray study on the conformation and structural properties of lupanine derivatives and salts in the solid state. Spectroscopic data (Wiewiórowski, Edwards & Bratek-Wiewiórowska, 1967) confirmed by X-ray analysis (Doucerain, Chiaroni & Riche, 1976) indicated a boat conformation for ring *C* of the lupanine molecule, both in the solid state and in solution. An interesting exception is 13-hydroxylupanine (Kałuski, Garbarczyk, Gusiev, Struchkov, Skolik & Wiewiórowski, 1977), where ring *C* adopts a chair conformation in the solid state, but the boat form in chloroform solution. As far as the stereochemistry of lupanine salts in solution is concerned it was previously suggested, on the basis of

the distortion of the tetrahedral angles around Zn²⁺ (Fig. 2).

References

- HAMILTON, W. C. & IBERS, J. A. (1968). *The Hydrogen Bond in Solids*. New York: Benjamin.
 JEFFREY, G. A. & KINOSHITA, Y. (1963). *Acta Cryst.* **16**, 20–28.
 KINDBERG, B. L. & AMMA, E. L. (1975). *Acta Cryst.* **B31**, 1492–1494.
 LANGRIDGE, R. & RICH, A. (1963). *Nature (London)*, **198**, 725–728.
 MARSH, R. E., BIENSTADT, R. & EICHHORN, E. L. (1962). *Acta Cryst.* **15**, 310–316.
 REEKE, G. N. JR & MARSH, R. E. (1966). *Acta Cryst.* **20**, 703–708.
 TAMURA, C., SATO, S. & HATA, T. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2388–2394.
 VOET, D. & RICH, A. (1969). *J. Am. Chem. Soc.* **91**, 3069–3075.

spectroscopic measurements (Wiewiórowski & Lompa-Krzemiń, 1969; Skolik, Barciszewski, Rafalski & Wiewiórowski, 1971), that N(16) protonation does not change the boat conformation of ring *C* in the lupanine skeleton. An X-ray analysis of (+)-lupanine hydrochloride dihydrate (Skrzypczak-Jankun & Kałuski, 1978) has shown that this conformation is also present in the solid state. Spectroscopic studies on other lupanine salts have indicated that in solution the anion does not significantly affect the configuration and conformation of the alkaloid skeleton (Wiewiórowski, Skolik & Perkowska, 1979). In order to find whether this statement also holds for the solid state, an X-ray study of (+)-lupanine perchlorate monohydrate has now been carried out. A further interesting point concerns the influence of the hydrogen-bonding network, and other intramolecular forces, on the conformation of ring *A*, containing the lactam group.

The title compound has been obtained and analysed by spectral methods by Skolik (1962). It was recrystallized from methanol and ether by vapour diffusion. A crystal 0.3 × 0.15 × 0.4 mm was used on the $P2_1$ Syntex diffractometer; 892 reflections were obtained of which 835 with $I > 1.96\sigma(I)$ were included in the calculations. The cell dimensions were obtained by a