

but all atoms of the acetyl group are significantly out of plane [$\Delta(\text{max.})$, 0.503(10) Å]. Nevertheless, C(9) is just 0.122(4) Å and O(11) just 0.032(3) Å out of plane, thereby maintaining a planar conjugation pathway O(1)–C(2)=C(3)–C(9)=O(11). A similar furan–carbonyl pathway, but with the formal double bonds *trans* rather than *cis*, has been reported in dimethyl 3a,4,9,9a-tetrahydro-9-oxo-*cis*-furo[3,2-*b*]quinoline-2,3-dicarboxylate (4) (Ueda, Ishiguro, Funakoshi, Saeki & Hamana, 1980). Bond distances, both for the five-atom conjugated systems and for the dihydrofuran moieties generally, agree closely in both molecules. Particularly noteworthy are the shortness of the O(1)–C(2) bond (present nomenclature, Ueda *et al.* values given second) [1.363(5) and 1.353(3) Å] and the angular deformations at C(3a) and C(2) [C(7a)–C(3a)–C(3), 102.5(3) and 100.5(2)°; O(1)–C(2)–C(3), 114.7(3) and 115.0(2)°; C(8)–C(2)–C(3), 132.7(5) and 131.3(2)°].

The four-atom C(3)-acetyl set exhibits a small pyramidal distortion with the central carbon [C(9)] displaced 0.018(4) Å from the C(3), C(10), O(11) plane. Such distortions are often associated with short O...C=O or N...C=O contacts (Bürgi, Dunitz & Shefter, 1973, 1974; Dunand & Robertson, 1982) and thought to typify points along the reaction pathway for nucleophilic attack (Bürgi *et al.*, 1973, 1974). No such interactions are apparent in the present compound, and

in this instance the deformation appears to be due to a series of weak intermolecular non-bonding interactions [O...H and O...C] to O(11).

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Dicytosinium Tetrachlorozincate, [C₄H₆N₃O]₂[ZnCl₄]

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Abstract. $M_r = 431.42$, triclinic, $P\bar{1}$, $a = 17.86(1)$, $b = 6.86(1)$, $c = 6.87(1)$ Å, $\alpha = 80.20(7)$, $\beta = 103.90(9)$, $\gamma = 101.63(6)^\circ$, $U = 794.1$ Å³, $Z = 2$, $D_m = 1.79(2)$, $D_x = 1.80$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.13$ mm⁻¹, $F(000) = 432$, $T = 298$ K. Final $R = 0.079$ for 4495 unique reflections. Each type of crystallographically unique cation is in a separate band in the structure. In one of these bands there is strong interaction between carbonyl groups of centrosymmetrically related cations. The bands are interleaved by tetrahedral tetrachlorozincate anions.

Introduction. This compound was isolated and its structure was determined in the course of a study of pyrimidine–metal-ion interactions.

Experimental. Excess, freshly precipitated zinc hydroxide, suspended in methanol, was added to cytosine dissolved in a 50:50 water:ethanol mixture and sufficient hydrochloric acid to clear the solution was added. After several days of slow evaporation colourless crystals with two different morphologies appeared; one type was identified as cytosine monohydrate and the other is the subject of this analysis. The crystals decomposed in air and were sealed in glass capillary tubes for all X-ray diffraction experiments.

The $\bar{1}$ diffraction symmetry obtained from precession photographs indicated that the crystal system was

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triclinic; unit-cell dimensions and intensity data measured on a Supper automatic two-circle diffractometer with graphite-monochromated $\text{MoK}\alpha$; unit-cell dimensions calculated from values of 2θ for 30 reflections in range $50 < 2\theta < 60^\circ$ obtained from the zero levels of two crystals mounted about the b and c axes; intensity data for 6946 reflections collected with $\theta/2\theta$ scan technique using one crystal mounted about \mathbf{b} [$0.25(1) \times 0.15(1) \times 0.10(1)$ mm] for layers $k = 0-3$ and another mounted about \mathbf{c} [$0.33(1) \times 0.25(1) \times 0.10(1)$ mm] for layers $l = 0-4$, absorption corrections not applied, intensities of reflections scaled and averaged (Rae, 1965) to give data for 4495 unique reflections; structure solved by using direct methods to locate the positions of Zn and Cl atoms and Fourier methods for the other atoms, and refined by full-matrix least-squares calculations minimizing $\sum w(\Delta F)^2$ where $w = \sigma^{-2}(F_o)$; values for $\sigma(F_o)$ were obtained from a combination of counting statistics and mean deviations for those reflections measured more than once, and counting statistics alone for the remainder; the positions of all H atoms were clearly defined in difference Fourier maps; scattering factors for Zn^{2+} , Cl^- , O, N, C, and H taken from *International Tables for X-ray Crystallography* (1974), curve used for H was that calculated by Stewart, Davidson & Simpson (1965), anomalous-dispersion corrections applied (Cromer & Liberman, 1970); parameters refined included a scale factor and positional and anisotropic temperature factor coefficients for the non-H atoms; H atoms were included at positions indicated by difference Fourier maps but their positional and isotropic thermal parameters were not refined, final $R = 0.079$, $wR = 0.065$ for the 4495 reflections included in the refinement; a final difference Fourier map showed no remarkable features, highest positive region $< 0.2 \text{ e } \text{\AA}^{-3}$; structure solved with *SHELX 76* (Sheldrick, 1976) and refined with the same set of programs.

Discussion. Final atomic coordinates are listed in Table 1, bond lengths and angles in Table 2.*

The crystal structure is dominated by bands of cytosinium cations, protonated at N(3), lying nearly parallel to (100), alternating with tetrachlorozincate(II) anions linking the adjacent bands together. The band near $x = 0$ is composed of one type of crystallographically unique cytosinium ions and the band near $x = \frac{1}{2}$ of the other type. Within these bands the cytosinium ions are linked by hydrogen bonds parallel to \mathbf{c} and by base stacking along \mathbf{b} (Fig. 1). There are no hydrogen bonds between bases in one band and bases in the other band. This overall arrangement of cations

and anions is very similar to that found in cytosinium hemitetrachlorozincate-cytosine (Fujinami, Ogawa, Arakawa, Shirotake, Fujii & Tomita, 1979), but within the cation bands the interbase interactions in the two structures are very different.

The arrangement of bases in the band at $x = 0$ (Fig. 2) is, however, nearly the same as that found for one

Table 1. Atomic coordinates and equivalent isotropic thermal parameters

| | x | y | z | $U_{eq}(\text{\AA}^2)$ |
|------------------------------|-------------|-------------|-------------|------------------------|
| $[\text{ZnCl}_4]^{2-}$ | | | | |
| Zn | 0.2615 (1) | 0.2336 (1) | -0.0538 (1) | 0.035 |
| Cl(1) | 0.2051 (1) | 0.5160 (3) | -0.1131 (3) | 0.042 |
| Cl(2) | 0.2628 (1) | 0.1177 (4) | -0.3395 (3) | 0.060 |
| Cl(3) | 0.3810 (1) | 0.2828 (3) | 0.1527 (3) | 0.040 |
| Cl(4) | 0.1855 (1) | -0.0231 (3) | 0.1152 (3) | 0.044 |
| Cytosinium ⁺ (I) | | | | |
| N(1) | 0.0861 (3) | 0.3530 (10) | 0.1869 (9) | 0.039 |
| C(2) | 0.0136 (4) | 0.2805 (13) | 0.0848 (12) | 0.043 |
| N(3) | -0.0426 (3) | 0.2145 (10) | 0.2011 (9) | 0.036 |
| C(4) | -0.0291 (4) | 0.2304 (11) | 0.4010 (11) | 0.033 |
| C(5) | 0.0475 (4) | 0.3146 (11) | 0.4979 (11) | 0.035 |
| C(6) | 0.1023 (4) | 0.3717 (12) | 0.3860 (12) | 0.039 |
| O(2) | -0.0023 (3) | 0.2683 (11) | -0.0953 (8) | 0.066 |
| N(4) | -0.0871 (3) | 0.1669 (10) | 0.4987 (9) | 0.041 |
| Cytosinium ⁺ (II) | | | | |
| N(1) | 0.5004 (3) | 0.2417 (10) | 0.8834 (10) | 0.042 |
| C(2) | 0.5752 (4) | 0.2326 (12) | 0.9964 (12) | 0.040 |
| N(3) | 0.6277 (3) | 0.2204 (9) | 0.8844 (9) | 0.034 |
| C(4) | 0.6127 (4) | 0.2262 (11) | 0.6822 (11) | 0.034 |
| C(5) | 0.5352 (4) | 0.2404 (12) | 0.5745 (11) | 0.039 |
| C(6) | 0.4816 (4) | 0.2465 (12) | 0.6809 (12) | 0.042 |
| O(2) | 0.5923 (3) | 0.2353 (10) | 1.1770 (8) | 0.058 |
| N(4) | 0.6681 (4) | 0.2166 (11) | 0.5926 (9) | 0.047 |

* U_{eq} is defined by Willis & Pryor (1975).

Table 2. Interatomic distances (\AA) and angles ($^\circ$) with their *e.s.d.*'s in parentheses

| ZnCl_4^{2-} | | ZnCl_4^{2-} | |
|----------------------|-----------|------------------------|-----------|
| Zn-Cl(1) | 2.292 (3) | Cl(1)-Zn-Cl(2) | 112.8 (1) |
| Zn-Cl(2) | 2.246 (3) | Cl(1)-Zn-Cl(3) | 110.9 (1) |
| Zn-Cl(3) | 2.258 (3) | Cl(1)-Zn-Cl(4) | 108.5 (1) |
| Zn-Cl(4) | 2.321 (3) | Cl(2)-Zn-Cl(3) | 112.8 (1) |
| | | Cl(2)-Zn-Cl(4) | 104.8 (1) |
| | | Cl(3)-Zn-Cl(4) | 106.5 (1) |
| | | CytH ⁺ (I) | |
| | | N(1)-C(2) | 1.36 (1) |
| | | C(2)-O(2) | 1.22 (1) |
| | | C(2)-N(3) | 1.39 (1) |
| | | N(3)-C(4) | 1.36 (1) |
| | | C(4)-N(4) | 1.33 (1) |
| | | C(4)-C(5) | 1.42 (1) |
| | | C(5)-C(6) | 1.34 (1) |
| | | N(1)-C(6) | 1.35 (1) |
| | | CytH ⁺ (II) | |
| | | C(2)-N(1)-C(6) | 122.8 (9) |
| | | N(1)-C(2)-O(2) | 123.5 (9) |
| | | N(1)-C(2)-N(3) | 115.5 (9) |
| | | O(2)-C(2)-N(3) | 121.0 (9) |
| | | C(2)-N(3)-C(4) | 123.7 (9) |
| | | N(3)-C(4)-N(4) | 119.3 (9) |
| | | N(3)-C(4)-C(5) | 118.0 (9) |
| | | N(4)-C(4)-C(5) | 122.6 (9) |
| | | C(4)-C(5)-C(6) | 118.0 (9) |
| | | N(1)-C(6)-C(5) | 121.9 (9) |

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38274 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

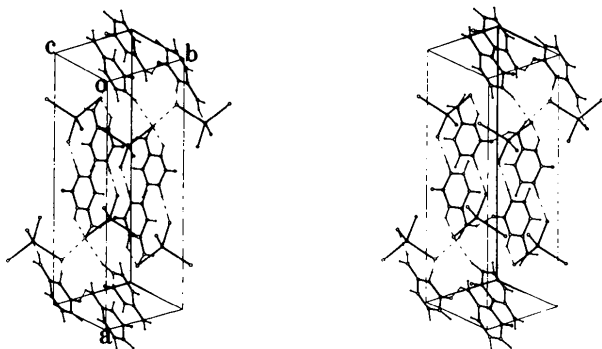


Fig. 1. A stereoscopic diagram of the structure drawn by *VIEW* (Carrell, 1979). Hydrogen bonds are shown as dashed lines.

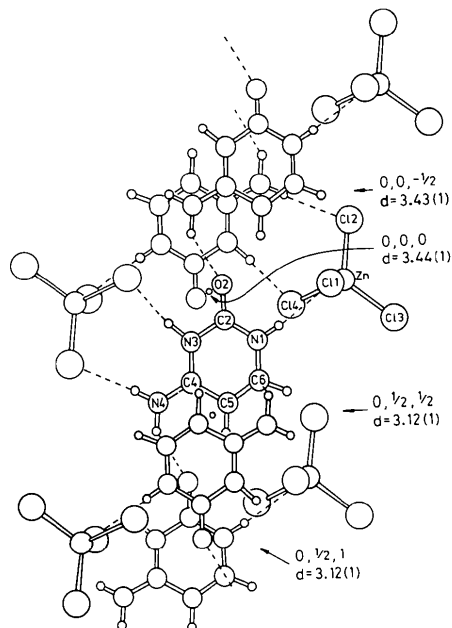


Fig. 2. The band of cytosinium⁺(I) cations viewed normal to the plane of the rings showing base stacking. Centres of symmetry are labelled with their fractional coordinates and *d* is the spacing (Å) between the least-squares planes of the pyrimidine rings related by that centre of symmetry. Hydrogen bonds are indicated by dashed lines between H and the acceptor atom. The coordinates of the labelled atoms correspond to those given in Table 1.

kind of cytosinium ions in dicytosinium tetrachlorocuprate(II) (Ogawa, Nishitani, Fujiwara, Shirotake & Tomita, 1979). There is a strong interaction in the region of the carbonyl groups of two molecules related by a centre of symmetry at $0, \frac{1}{2}, 0$ (shown as $0, \frac{1}{2}, 1$ in Fig. 2). In this region the distances of the least-squares plane through N(1), C(2), N(3), C(4),

C(5), and C(6) to C(2) and O(2) of a centrosymmetrically related molecule are 3.09 (1) and 3.06 (1) Å respectively, distances that are similar to those in the cuprate analogue. Another close interaction is found about 0,0,0 where the spacing between the least-squares planes of the purine rings is 3.12 (1) Å. The bases in this band are connected in chains by N(4)—H...O(2) hydrogen bonds [2.96 (1) Å] as in the cuprate analogue. The bases near $x = \frac{1}{2}$ are further from the centres of symmetry and do not overlap to a significant extent. They are connected in chains by N(4)—H...O(2) hydrogen bonds [2.84 (1) Å] and are hydrogen-bonded to the anions. The arrangement of bases in this band is therefore not the same as that in the cuprate analogue.

The existence of nearly identical bands of cytosinium cations in the cuprate and zincate analogues is an indication that this is a stable arrangement. The different arrangement in the second band is presumably a consequence of different packing requirements of the nearly regular tetrahedral tetrachlorozincate ions on the one hand and the flattened tetrahedral tetrachlorocuprate ions on the other.

The H atoms on N(1), N(3) and one on N(4) are all involved in N—H...Cl hydrogen bonds. These bonds range in length (N...Cl) from 3.149 (8) to 3.386 (8) Å with N—H...Cl angles ranging from approximately 146 to 176°.

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