

Bis(6-thioxo-1,6-dihydropurinium) tetrachlorozincate(II)

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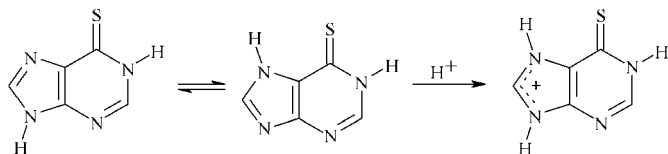
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The title salt, $(C_5H_5N_4S)_2[ZnCl_4]$, consists of two 6-thioxo-1,6-dihydropurinium ($6mpH_2^+$) cations (*A* and *B*) and a tetrachlorozincate anion, which are held together by $N-H \cdots Cl$ and $C-H \cdots Cl$ interactions. There is an anion- π interaction between one Cl atom of the $[ZnCl_4]^-$ anion and the pyrimidine ring of the $6mpH_2^+(B)$ cation. Intermolecular $\pi-\pi$ stacking interactions allow $6mpH_2^+(A)$ cations to form antiparallel pairs. One interesting structural feature is the double $N-H \cdots N$ intermolecular hydrogen bonds between two $6mpH_2^+(A)$ cations. This kind of interaction, mimicking that of natural nucleobases, can be very valuable in designing new therapeutic purine derivatives.

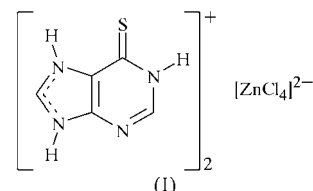
Comment

6-Mercaptopurine ($6mpH$; 1,7-dihydro-6*H*-purine-6-thione) exists in solid and liquid states in the 6-thione form. It also has a tautomeric imine proton equilibrium between positions 7 and 9 of the imidazole ring (Pazderski *et al.*, 2006), being found in the $N9-H$ form in anhydrous $6mpH$ (Gyr, 1991) but in the $N7-H$ form in 6-mercaptopurine monohydrate (see the reaction scheme below) (Sletten *et al.*, 1969; Brown, 1969). The 6-thioxo-1,6-dihydropurinium cation ($6mpH_2^+$), in which both the $N7$ and the $N9$ positions are protonated and the positive charge is shared by the imidazole N atoms, was previously confirmed by single-crystal X-ray diffraction and vibrational spectroscopy of 6-thioxo-1,6-dihydropurinium chloride (Perez-Ruiz *et al.*, 1998).



Preparation and structural characterization of complexes of biologically active metals, such as zinc, with purines is one of our recent interests. In an attempt to prepare the zinc analogue of bis(6-mercaptopurinato)mercury(II) (Lavertue *et al.*, 1976), we obtained to the title salt, (I).

There are two crystallographically independent planar $6mpH_2^+$ cations and one tetrachlorozincate anion in the asymmetric unit (Fig. 1). The pyrimidine H atoms of the $6mpH_2^+$ cations (*A* and *B*) are involved in $N1-H \cdots Cl3$ and $N21-H \cdots Cl2$ hydrogen bonds, respectively, the latter being much weaker (Desiraju & Steiner, 1999), as seen from Table 2. There is also a weak short $C-H \cdots Cl$ contact between atoms $C2$ and $Cl2$, generating an $R_2^2(7)$ graph-set motif (Bernstein *et al.*, 1995) with the $N1-H \cdots Cl3$ hydrogen bond.



$6mpH_2^+$ cations can form pairs in the crystalline state, regardless of the electrostatic force between their positive charges. Repulsion of similar charges is reduced by antiparallel geometry, and the cations are held together by $\pi-\pi$ stacking and possibly also by cation- π interactions (Meyer *et al.*, 2003). Such a pair of antiparallel-displaced $6mpH_2^+(A)$ cations is shown in Fig. 2, around $(\frac{1}{2}, \frac{1}{2}, 1)$, with an interplanar distance of 3.447 (3) Å. The centroid-to-centroid distance of the six-membered aromatic rings is 3.584 (3) Å. Cation- π interactions in this pair may also exist, but because of the partial overlap of the $6mpH_2^+(A)$ cations with positive charges at two ends, such interactions are not favoured. There is no $6mpH_2^+(B)$ pair that has a rational centroid-to-centroid distance, but the $6mpH_2^+(B)$ cation participates in an anion- π interaction with atom $Cl1$ (Fig. 1). The distance between the centroid of the pyrimidine ring and atom $Cl1$ is 3.247 (3) Å, which is slightly longer than that observed in the 1,3,5-triazine complex (Demeshko *et al.*, 2004). The angle between the $Cl1 \cdots$ centroid axis and the plane of the pyrimidine ring is 85° , and the $Cl1 \cdots$ centroid axis points away from atoms $N21$ and $N23$.

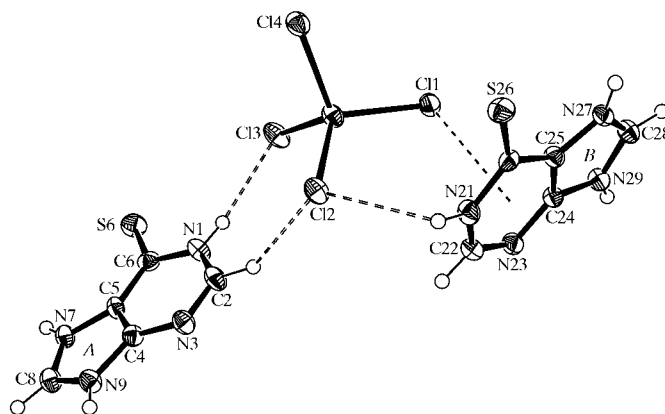


Figure 1
The $6mpH_2^+$ and $[ZnCl_4]^{2-}$ components of (I), showing the atom-labelling scheme. Displacement ellipsoids were drawn at the 50% probability level and non-covalent interactions are illustrated with dashed lines.

Previous studies of tetrachlorozincates have shown that the Zn—Cl bond lengths are not identical (Parvez & Sabir, 1998; García-Raso *et al.*, 1999). The environment around the anion, for example, the presence of hydrogen bonds or repulsions, influences appreciably the Zn—Cl bond lengths and Cl—Zn—Cl angles. In (I), however, no clear trend of such influences was detected (Table 1). For example, the fact that the Zn—Cl4 bond is the longest does not meet the expectations derived from hydrogen-bonding effects (Table 2), because atom Cl4 accepts only one, rather weak, N—H...Cl contact.

Imidazole atoms N7 and N9 of the 6mpH₂⁺ cation share the positive charge (Perez-Ruiz *et al.*, 1998). Therefore, the bonds involving atoms N7, N9, N27 and N29 in (I) are expected to be of about equal length. The N7—C8 and N27—C28 bonds (Table 1) are comparable to the N7—C8 distance in 6mpH₂Cl (Pazderski *et al.*, 2006), and the N9—C8 and N29—C28 bonds are slightly longer than the N7—C8 and N27—C28 bonds. However, all of these bond lengths in (I) are closer to one another than the analogous bonds in 6mpH·H₂O and in anhydrous 6mpH (Pazderski *et al.*, 2006; Gyr, 1991). One interesting structural feature involving the imidazole N atoms is the double N9—H9...N3ⁱⁱ intermolecular hydrogen-bond system (Table 2) between two 6mpH₂⁺(A) cations (shown at the centre of Fig. 2), generating an R₂²(8) graph-set motif. These cations are in the same plane and related by an inversion centre.

Sulfur is a weak atomic acceptor and it is often superseded in hydrogen-bond formation because of the presence of stronger acceptors (Desiraju & Steiner, 1999). Certainly, some such interactions, *e.g.* N—H...S (Dubler & Gyr, 1988) and C—H...S (Cini *et al.*, 2000), have been reported for 6mpH compounds, but they are rather unusual. In (I), there is possibly a very weak C28—H28...S26^v interaction (Table 2). Atom S26 also forms a short contact [3.3929 (12) Å] to Cl4 at ($-x, \frac{1}{2} + y, \frac{3}{2} - z$), which is shorter than the sum of van der Waals radii (3.55 Å).

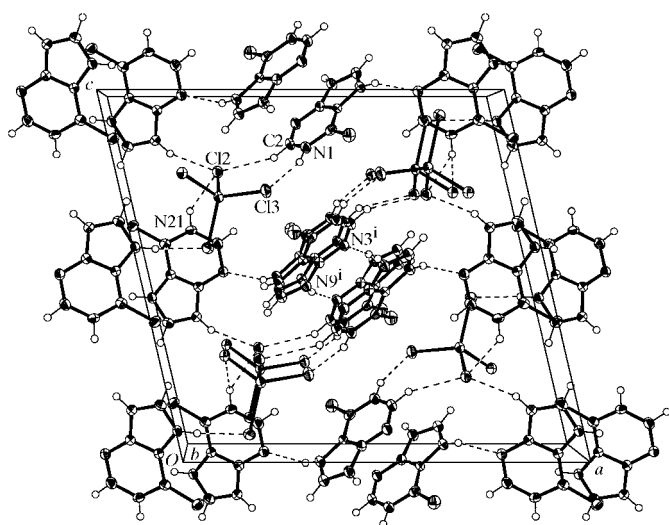


Figure 2

The packing of (I), viewed along the *b* axis. Hydrogen bonds are illustrated with dashed lines. [Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$]

Experimental

6-Mercaptopurine monohydrate (119 mg, 0.70 mmol) and zinc chloride (48 mg, 0.35 mmol) were dissolved in water (50 ml). The mixture was stirred at room temperature for one hour, after which aqueous 2 M HCl (20 ml) was added and the resulting solution was left to stand. After one week, some crystals and a pale-yellow powder were formed, and these were removed from the solution; the powder was found to be mostly 6-thioxo-1,6-dihydropurinium chloride, and the crystals were found to be 6-mercaptopurine monohydrate. After slow evaporation of the solution at room temperature over a period of three months, only a few colourless crystals of (I) were obtained. A similar synthetic route was tested unsuccessfully with cobalt(II) and cadmium(II) chlorides.

Crystal data

| | |
|--|---|
| (C ₅ H ₅ N ₄ S) ₂ [ZnCl ₄] | <i>Z</i> = 4 |
| <i>M_r</i> = 513.55 | <i>D_x</i> = 1.851 Mg m ⁻³ |
| Monoclinic, <i>P</i> 2 ₁ / <i>c</i> | Mo <i>K</i> α radiation |
| <i>a</i> = 17.1397 (5) Å | <i>μ</i> = 2.15 mm ⁻¹ |
| <i>b</i> = 6.8500 (2) Å | <i>T</i> = 173 (2) K |
| <i>c</i> = 16.1142 (5) Å | Block, colourless |
| <i>β</i> = 103.021 (2)° | 0.25 × 0.15 × 0.15 mm |
| <i>V</i> = 1843.27 (10) Å ³ | |

Data collection

| | |
|--|---|
| Bruker Kappa-APEX-II diffractometer | 27322 measured reflections |
| <i>φ</i> and <i>ω</i> scans | 4528 independent reflections |
| Absorption correction: multi-scan (MULABS in PLATON; Blessing, 1995; Spek, 2003) | 3408 reflections with <i>I</i> > 2σ(<i>I</i>) |
| <i>T_{min}</i> = 0.603, <i>T_{max}</i> = 0.724 | <i>R_{int}</i> = 0.087 |
| | <i>θ_{max}</i> = 28.3° |

Refinement

| | |
|-------------------------------------|---|
| Refinement on <i>F</i> ² | $w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 3.7658P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.046$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.084$ | (Δ/σ) _{max} = 0.001 |
| <i>S</i> = 1.05 | $\Delta\rho$ _{max} = 0.44 e Å ⁻³ |
| 4528 reflections | $\Delta\rho$ _{min} = -0.44 e Å ⁻³ |
| 226 parameters | |
| H-atom parameters constrained | |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-------------|-------------|------------|
| Zn1—Cl1 | 2.2547 (9) | N7—C8 | 1.323 (4) |
| Zn1—Cl2 | 2.2776 (10) | N9—C8 | 1.339 (4) |
| Zn1—Cl3 | 2.2750 (9) | N9—C4 | 1.368 (4) |
| Zn1—Cl4 | 2.2861 (9) | C24—C25 | 1.368 (4) |
| S6—C6 | 1.647 (4) | N27—C25 | 1.378 (4) |
| S26—C26 | 1.655 (3) | N27—C28 | 1.321 (4) |
| C4—C5 | 1.374 (4) | N29—C28 | 1.334 (4) |
| N7—C5 | 1.383 (4) | N29—C24 | 1.368 (4) |
| Cl1—Zn1—Cl3 | 109.44 (4) | Cl1—Zn1—Cl4 | 109.33 (3) |
| Cl1—Zn1—Cl2 | 114.54 (4) | Cl3—Zn1—Cl4 | 107.60 (4) |
| Cl3—Zn1—Cl2 | 110.12 (3) | Cl2—Zn1—Cl4 | 105.54 (4) |

All H atoms were found in difference density maps, but were placed in ideal calculated positions and allowed to ride on their parent atoms at distances of 0.88 (N—H) and 0.95 Å (C—H), with *U*_{iso}(H) values of 1.2*U*_{eq}(C,N).

Data collection: COLLECT (Bruker, 2004); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SIR2002 (Burla *et al.*, 2003); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia,

Table 2
Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1...Cl3 | 0.88 | 2.34 | 3.180 (3) | 159 |
| N21—H21...Cl2 | 0.88 | 2.76 | 3.245 (3) | 116 |
| N7—H7...N23 ⁱ | 0.88 | 2.01 | 2.811 (4) | 151 |
| N9—H9...N3 ⁱⁱ | 0.88 | 2.00 | 2.857 (4) | 163 |
| N21—H21...Cl4 ⁱⁱⁱ | 0.88 | 2.45 | 3.216 (3) | 146 |
| N27—H27...Cl1 ^{iv} | 0.88 | 2.31 | 3.184 (3) | 174 |
| N29—H29...Cl2 ^v | 0.88 | 2.30 | 3.134 (3) | 159 |
| C2—H2...Cl2 | 0.95 | 2.58 | 3.432 (3) | 149 |
| C8—H8...Cl4 ^{vi} | 0.95 | 2.61 | 3.540 (3) | 165 |
| C28—H28...S26 ^v | 0.95 | 2.78 | 3.556 (4) | 140 |

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, -y + 2, -z + 2$; (iii) $x, y + 1, z$; (iv) $-x, -y + 1, -z + 1$; (v) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $-x + 1, -y + 1, -z + 2$.

1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3005). Services for accessing these data are described at the back of the journal.

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