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5-Methylsulfanyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7(6*H*)-one (2-methylthio-8-azaxanthine) monohydrate

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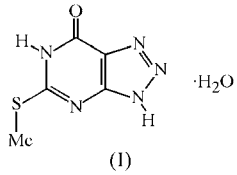
The title compound, $C_5H_5N_5OS\cdot H_2O$, crystallizes as the monohydrate. Disorder of the H atoms that participate in the hydrogen bonds implies that two different tautomers are present in the crystal structure, one of them with both acidic H atoms attached to the imidazole ring and the other with one acidic H atom on each ring.

Comment

Triazolopyrimidine compounds exhibit a wide spectrum of biological activities and versatile coordination properties. The interaction of metal ions with 1,2,4-triazolo[1,5-*a*]pyrimidine derivatives has been extensively investigated by our research group and a number of papers have been reported (Salas *et al.*, 1999). Recently, we have started to explore the coordination possibilities of other triazolopyrimidines, such as 1,2,4-triazolo[4,3-*a*]pyrimidines, which differ from the triazolo[1,5-*a*]-pyrimidine derivatives by the position of one N atom in the triazole ring (Salameh *et al.*, 2005). 1,2,3-Triazolo[4,5-*d*]pyrimidines, which contain three contiguous N atoms in the imidazole ring, represent yet another way of joining a triazole and a pyrimidine ring. These compounds may also be regarded as purine derivatives, replacing the external C atom of the imidazole ring with an N atom. For this reason, these compounds may also be named as 8-azapurines, using a biochemical instead of a systematic IUPAC numbering scheme.



(I)

Several crystal structures have been reported for this family of ligands (Sánchez *et al.*, 1995, and references therein), as well as for some of their metal complexes (Ravichandran *et al.*, 1986; Sheldrick & Bell, 1986). Most of these results were published prior to 1990, with very few of them having been published in the last 25 years. Revisiting this research area, this paper describes the crystal structure of a member of the family which has a methylsulfanyl group at position 5, namely 5-methylsulfanyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7(6*H*)-one monohydrate, (I), which may also be named as a substituted purine using the biochemical numbering scheme, *i.e.* 2-methylthio-8-azaxanthine. However, the systematic IUPAC name and numbering scheme have been used throughout this paper and are displayed in Figs. 1 and 2.

Compound (I) crystallizes as the monohydrate and the asymmetric unit is made up of just one organic moiety and a water molecule. A hydrogen bond is formed between two crystallographically equivalent water molecules related by a binary axis [$O1W\cdots O1W^{i} = 2.717\ (5)$ Å; symmetry code: $1-x, y, -z+\frac{1}{2}$]. The corresponding H atom, which was located in a ΔF map, has been forcibly disordered between two equivalent positions close to the binary axis. In one position the water molecule acts as an H-atom donor and in the other it acts as an acceptor of the $O1W\cdots O1W^{i}$ hydrogen bond. The water molecule also forms hydrogen bonds with atom N6 in the same asymmetric unit and atom N1 of an adjacent molecule at $(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ [distances of 2.768 (4) and 2.844 (4) Å, respectively]. Two weak peaks were found in each of these two $O\cdots N$ regions, one close to O and the other close to N. This has been rationalized using two superimposed hydrogen-bonding schemes. When the water molecule acts as a donor of the $O1W\cdots O1W^{i}$ hydrogen bond, it also acts as a donor for the $O1W\cdots N1$ hydrogen bond and an acceptor of the $O1W\cdots N6$ hydrogen bond. The scheme is reversed when the water molecule acts as the acceptor of the $O1W\cdots O1W^{i}$ hydrogen bond.

This implies that the organic molecule of (I) is disordered between two tautomers, one with a H atom attached to atom N6 and the other with a H atom attached to atom N1. These two tautomers are depicted in Figs. 1 and 2, respectively. Both hydrogen-bonding schemes, including the corresponding tautomers for the heterocycle, and the relation between them are represented in Fig. 3. In both cases, the remaining acidic H atom is clearly located on atom N3, forming a hydrogen bond

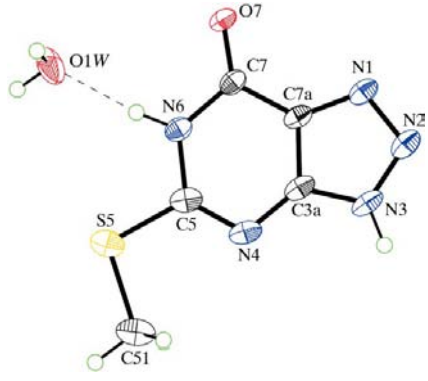


Figure 1
A view of the asymmetric unit of (I), considered as the N6—H tautomer (see *Comment*). Displacement ellipsoids are drawn at the 50% probability level.

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with the carbonyl O atom of the molecule at $(x, 1-y, \frac{1}{2}+z)$ [distance 2.692 (3) Å]. To our knowledge, the N1 tautomer is the only example with two acidic H atoms on the imidazole ring for this family of compounds.

Tautomerism is an interesting feature of these compounds, examples with one acidic H atom at each of the three imidazole N atoms having been found previously (Sánchez *et al.*, 1995). The presence of a H atom is reflected by an opening of the corresponding endocyclic angle, comparable with the change observed when a substituent such as a methyl group is attached to an imidazole N atom (Cline & Hodgson, 1980). Endocyclic bond angles in the imidazole ring in compound (I) (Table 1) follow this trend, with the values at N1 and N3 analogous to those of compounds with H atoms or substituents at these positions and the value at N2 analogous to those of compounds with a naked N atom at that position (Cline & Hodgson, 1980; Sánchez *et al.*, 1995). The methylsulfanyl group is almost coplanar with the heterocycle [torsion angle N4—C5—S—CH_3 = 0.8 (3)°].

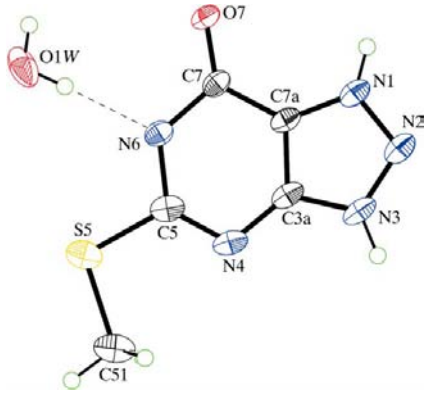

Figure 2
A view of the asymmetric unit of (I), considered as the N1—H tautomer (see *Comment*). Displacement ellipsoids are drawn at the 50% probability level.

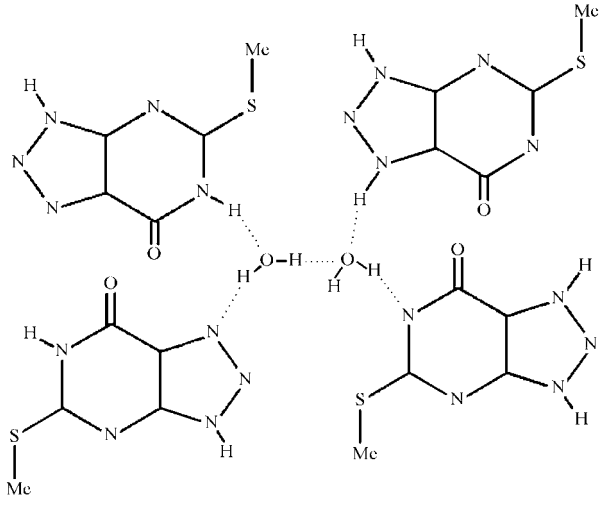

Figure 3
A disorder scheme for the hydrogen bonds. Both water molecules at the centre of the drawing are related by a crystallographic binary axis. One of the alternative positions for the H atoms is represented on the left-hand side of the drawing (including the N6—H tautomer) and the other on the right-hand side (including the N1—H tautomer).

Experimental

The synthesis of (I) was carried out according to the published method of Nübel & Pfleiderer (1965). Glacial acetic acid (2 mmol) and solid $NaNO_2$ (2 mmol) were added to an aqueous solution (*ca* 25 ml) of 5,6-diamino-4-hydroxy-2-(methylsulfanyl)pyrimidine (1 mmol). The mixture was allowed to evaporate at room temperature and, after 5 d, yellow prismatic crystals of the title compound were obtained. Elemental analysis reveals that the compound crystallizes as the monohydrate. Analysis found: C 29.20, H 3.44, N 34.98%; calculated: C 29.85, H 3.51, N 34.81%.

Crystal data

$C_5H_5N_5OS\cdot H_2O$
M_r = 201.22
Monoclinic, $C2/c$
a = 17.1216 (12) Å
b = 7.3269 (5) Å
c = 14.3494 (10) Å
β = 113.259 (1)°
V = 1653.8 (2) Å^3
Z = 8
D_x = 1.616 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 100 (2) K
Prismatic, yellow
0.53 × 0.25 × 0.17 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.806, T_{max} = 0.940
5011 measured reflections
1886 independent reflections
1799 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 28.1°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.126
S = 1.28
1886 reflections
131 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.015P)^2 + 7P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.008
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.309 (3)	C5—N6	1.380 (3)
N1—C7a	1.358 (4)	C5—S5	1.743 (3)
N2—N3	1.360 (4)	S5—C51	1.803 (3)
N3—C3a	1.345 (4)	N6—C7	1.394 (4)
C3a—N4	1.361 (4)	C7—O7	1.231 (3)
C3a—C7a	1.381 (4)	C7—C7a	1.430 (4)
N4—C5	1.311 (4)		
N2—N1—C7a	108.0 (2)	N6—C5—S5	112.7 (2)
N1—N2—N3	107.8 (2)	C5—S5—C51	101.17 (16)
C3a—N3—N2	110.7 (2)	C5—N6—C7	124.5 (2)
N3—C3a—N4	128.2 (2)	O7—C7—N6	121.8 (2)
N3—C3a—C7a	103.9 (3)	O7—C7—C7a	127.0 (3)
N4—C3a—C7a	128.0 (3)	N6—C7—C7a	111.3 (2)
C5—N4—C3a	111.9 (2)	N1—C7a—C3a	109.5 (2)
N4—C5—N6	124.9 (3)	N1—C7a—C7	131.2 (3)
N4—C5—S5	122.4 (2)	C3a—C7a—C7	119.3 (3)

Methyl H atoms were idealized, allowing for free rotation around the N—C bond. H atoms attached to the N atoms in positions 3, 1 and

6 were introduced in ideal positions, the first with full occupancy and the last two with half-occupancy (peaks in the ΔF maps with appropriate intensity appeared before the introduction of these atoms). Four residual peaks around the water O atom with correct positions for hydrogen bonding and reasonable angles for considering the water molecule as disordered between two positions were introduced as half-occupancy H atoms and refined with restrained O—H [0.84 (1) Å] and H···H [1.33 (1) Å] distances. The isotropic displacement parameters of all H atoms were fixed at 1.2 times the U_{eq} values of their parent atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 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: HJ3007). Services for accessing these data are described at the back of the journal.

References

Bruker (1999). *SADABS* (Version 2.05), *SMART* (Version 5.624) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
Cline, S. J. & Hodgson, D. J. (1980). *J. Am. Chem. Soc.* **102**, 6285–6288.
Hall, S. R. & du Boulay, D. (1997). *Xtal_GX*. University of Western Australia, Australia.
Nübel, G. & Pfleiderer, W. (1965). *Chem. Ber.* **98**, 1060–1072.
Ravichandran, V., Ruban, G. A., Chacko, K. K., Molina, M. A. R., Rodríguez, E. C., Salas-Peregrín, J. M., Aoki, K. & Yamazaki, H. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1780–1782.
Salameh, S., Abul-Haj, M., Quirós, M. & Salas, J. M. (2005). *Eur. J. Inorg. Chem.* pp. 2779–2782.
Salas, J. M., Romero, M. A., Sánchez, M. P. & Quirós, M. (1999). *Coord. Chem. Rev.* **195**, 1119–1142.
Sánchez, M. P., Romero, M. A., Salas, J. M., Cárdenas, D. J., Molina, J. & Quirós, M. (1995). *J. Mol. Struct.* **344**, 257–264.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, W. S. & Bell, P. (1986). *Inorg. Chim. Acta*, **123**, 181–187.