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Two hydrates of 6-methoxypurine

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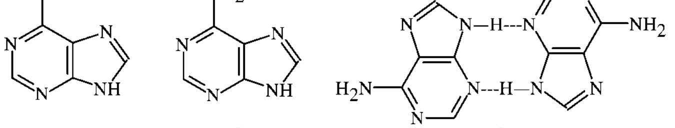
6-Methoxypurine crystallizes from *N*,*N*-methylformamide as the hemihydrate, $C_6H_6N_4O\cdot0.5H_2O$, and from water as the trihydrate, $C_6H_6N_4O\cdot3H_2O$. Both forms crystallize in the triclinic crystal system. Upon heating the trihydrate, molecules of water are liberated successively; the hemihydrate is formed at 383 K. In the hemihydrate, the H atom on the imidazole N atom is disordered between the two N atoms. The water molecule in the hemihydrate and the H atoms of a water molecule in the trihydrate are also disordered. In the hemihydrate, the organic moieties are connected by $N-H\cdots N$ hydrogen bonds, while they are connected *via* water molecules in the trihydrate.

Comment

6-Methoxypurine, (1), has been examined because of its ability to undergo methyl rearrangement in the solid or liquid state (Kaftory & Handelsman-Benory, 1994; Handelsman-Benory *et al.*, 2000; Greenberg *et al.*, 2001; Kaftory *et al.*, 2001; Kaftory, 2002). We have therefore investigated the structure and thermal behavior of commercially available 6-methoxypurine hemihydrate. Attempts to crystallize the hemihydrate of (1) from water failed, and a trihydrate form was obtained. Later, it was found that the hemihydrate can be crystallized from *N*,*N*-methylformamide. The crystal structures and the thermal behavior of the two hydrates are described below.



(1) (2) (3)

(I) = $(1)\cdot0.5H_2O$
(II) = $(1)\cdot3H_2O$

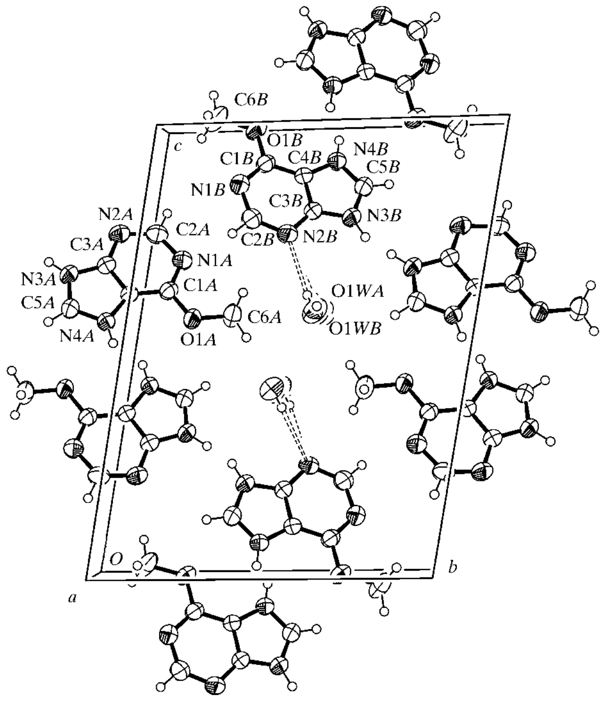


Figure 1
The crystal packing of molecules of hemihydrate (I) in the unit cell. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

The structures of the hemihydrate, (I), and trihydrate, (II), showing the atomic numbering and hydrogen bonding, are given in Figs. 1 and 2, respectively. 6-Methoxypurine was expected to pack in a similar way to aminopurine, (2) (Serra *et al.*, 1992), which forms dimers, (3), held together by hydrogen bonds, as shown in the scheme above. However, 6-methoxypurine crystallizes either with half a molecule or with three molecules of water. 6-Methoxypurine hemihydrate, (I), crystallizes with two symmetry-independent molecules (*A* and *B*) in the asymmetric unit. The water molecule is hydrogen bonded to the organic moiety, while the organic moieties are

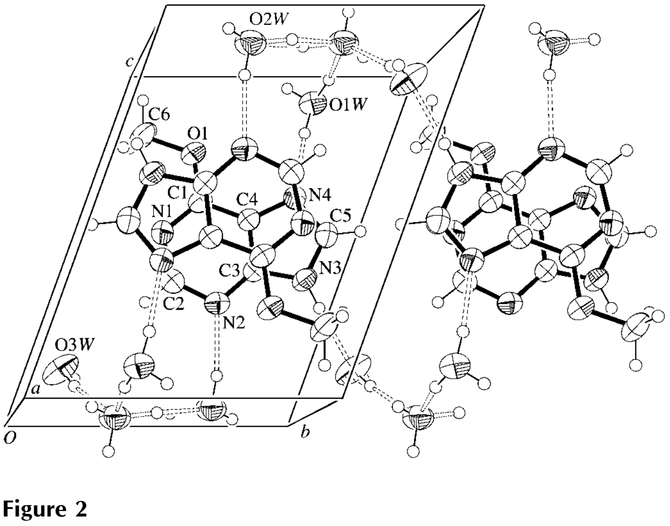


Figure 2
The crystal packing of molecules of trihydrate (II) in the unit cell. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

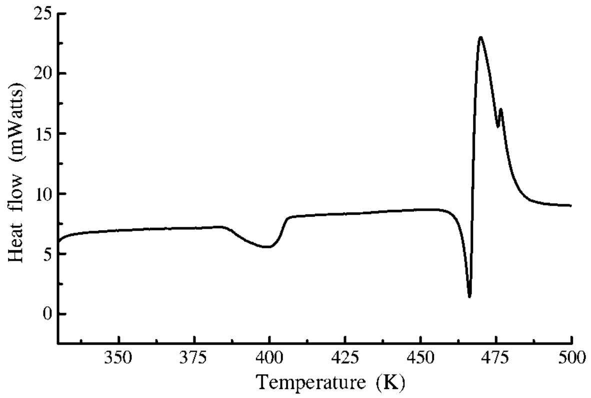


Figure 3
A DSC thermogram for hemihydrate (I) (heating rate 5 K min^{-1}, weight 7.8 mg).

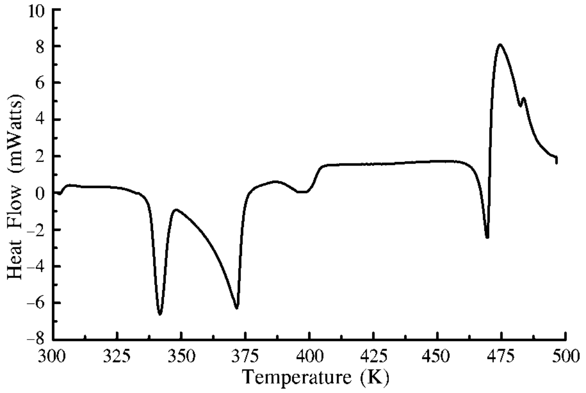


Figure 4
A DSC thermogram for trihydrate (II) (heating rate 5 K min^{-1}, weight 3.4 mg).

linked to one another *via* N—H···N hydrogen bonds (Table 1 and Fig. 1). The water molecule is disordered over two sites with equal occupancies, as is the amino H atom (H3), which is equally distributed between atoms N3 and N4. The disorder is also expressed by the similar lengths of the N3—C5 and N4—C5 bonds (Table 3). Formally, one bond should be a single and the other a double bond. However, the experimental distances are 1.339 (3) and 1.328 (3) Å [in molecule *A* of (I)], and 1.331 (3) and 1.320 (3) Å (in molecule *B*), while in 6-methoxypurine trihydrate, (II), these distances are 1.348 (2) and 1.321 (2) Å for the single and double bonds, respectively. In the crystal structure of (II), the water molecules serve as linkers between the organic molecules, *via* hydrogen bonding. There are nine strong hydrogen bonds, of which six are between the water molecules, and three are between molecules of water and the organic moiety (Table 2 and Fig. 2). One of the water molecules is disordered.

The thermal behavior of (I) is indicated by the DSC (differential scanning calorimetry) thermograph shown in Fig. 3. The thermograph consists of two single endotherms. The first endothermic peak is assigned to the liberation of molecules of water at 399 K ($\Delta H = 11.08$ kJ mol^{-1}), the second endothermic peak (at 466 K, $\Delta H = 5.27$ kJ mol^{-1}) is assigned to the melting point, and the last exothermic peak (at 470 K, $\Delta H = -33.06$ kJ mol^{-1}) is assigned to the methyl rearrangement in the liquid state. The DSC thermographs of (I) and (II) (Fig. 4) are identical in the temperature range 383–493 K, but the thermograph of (II) includes two additional endothermic peaks at lower temperatures. These extra peaks are assigned to the liberation of two crystallographically non-identical molecules of water, one liberated at 342 K ($\Delta H_1 = 21.84$ kJ mol^{-1}) and the second liberated at 372 K ($\Delta H_2 = 44.71$ kJ mol^{-1}).

Experimental

6-Methoxypurine was obtained from a commercial source (Aldrich) and was used without further purification. Needle-shaped crystals of (I) were grown from *N*,*N*-methylformamide and plate-like crystals of (II) were obtained from water.

Hemihydrate (I)

Crystal data

$C_6H_6N_4O \cdot 0.5H_2O$
$M_r = 158.91$
Triclinic, $P\overline{1}$
$a = 3.898$ (1) Å
$b = 11.966$ (2) Å
$c = 15.945$ (3) Å
$\alpha = 79.08$ (2)°
$\beta = 83.54$ (2)°
$\gamma = 87.09$ (2)°
$V = 725.3$ (3) Å^3
$Z = 4$
$D_x = 1.455$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2579 reflections
$\theta = 1.3$–25.1°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.30 × 0.12 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
2579 measured reflections
2574 independent reflections
1877 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.000$
$\theta_{\rm max} = 25.1$°
$h = -4 \rightarrow 0$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.125$
$S = 1.03$
2574 reflections
227 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.0856P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4*A*—H4*A*···N4*A*$^{\rm i}$	0.86	1.95	2.801 (3)	171
N3*A*—H3*A*···N3*B*$^{\rm ii}$	0.86	1.95	2.794 (3)	167
N4*B*—H4*B*···N4*B*$^{\rm iii}$	0.86	1.94	2.791 (3)	173
N3*B*—H3*B*···N3*A*$^{\rm iv}$	0.86	1.98	2.794 (3)	158
O1*WB*—H1*WA*···N2*B*$^{\rm v}$	0.77	2.30	3.021 (3)	157

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $x, y - 1, z$; (iii) $-x, 1 - y, 2 - z$; (iv) $x, 1 + y, z$; (v) $x - 1, y, z$.

Acta Cryst. (2004). C**60**, o44–o46 Natalya Fridman *et al.* • $C_6H_6N_4O \cdot 0.5H_2O$ and $C_6H_6N_4O \cdot 3H_2O$ **o45**

Trihydrate (II)

Crystal data

$C_6H_6N_4O{\cdot}3H_2O$
$M_r = 204.20$
Triclinic, $P\overline{1}$
$a = 6.8370\ (10)$ Å
$b = 7.819\ (2)$ Å
$c = 10.281\ (2)$ Å
$\alpha = 70.13\ (2)^\circ$
$\beta = 75.49\ (2)^\circ$
$\gamma = 80.29\ (2)^\circ$
$V = 498.29\ (18)$ Å^3
$Z = 2$
$D_x = 1.361$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3048 reflections
$\theta = 2.2$–25.0°
$\mu = 0.11$ mm^{-1}
$T = 293\ (2)$ K
Plate, colorless
0.40 × 0.30 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
3048 measured reflections
1765 independent reflections
1244 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 25.0^\circ$
$h = -8 \rightarrow 7$
$k = -9 \rightarrow 8$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.094$
$S = 0.92$
1765 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.024$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3N···O3$W^{\rm iv}$	0.86	1.88	2.735 (2)	174
O1W—H1WA···N4	0.94 (3)	1.89 (3)	2.816 (2)	173 (2)
O1W—H1WB···O2$W^{\rm vi}$	1.11	1.66	2.759 (2)	170
O1W—H1WC···O1$W^{\rm iii}$	0.84	1.96	2.801 (2)	174
O2W—H2WA···N2$^{\rm vii}$	0.90 (3)	1.95 (3)	2.838 (2)	169 (2)
O2W—H2WB···O2$W^{\rm vi}$	1.10	1.81	2.815 (2)	150
O3W—H3WB···O2$W^{\rm viii}$	0.87 (3)	1.91 (3)	2.770 (2)	172 (2)
O3W—H3WA···O1$W^{\rm ix}$	0.88 (3)	1.91 (3)	2.783 (2)	177 (2)

Symmetry codes: (iii) $-x, 1-y, 2-z$; (iv) $x, 1+y, z$; (vi) $1-x, 1-y, 2-z$; (vii) $1-x, 1-y, 1-z$; (viii) $x, y, z-1$; (ix) $-x, 1-y, 1-z$.

Both structures are disordered and therefore the refinement did not converge satisfactorily. The most difficult aspect was the refinement of the disordered water molecules. In (I), the water molecules equally occupy two sites and the O atoms refined satisfactorily. One of the H atoms of each water molecule occupies the same site, and therefore it has full occupancy and refines well. However, only one of the other two H atoms, with an occupancy of 0.5, could be detected and refined. In (II), there are two water molecules that are rotationally disordered, in which one of the H atoms has full occupancy, while the second is disordered over two sites.

For both hydrates, data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1151). Services for accessing these data are described at the back of the journal.

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o46 Natalya Fridman *et al.* • $C_6H_6N_4O{\cdot}0.5H_2O$ and $C_6H_6N_4O{\cdot}3H_2O$ *Acta Cryst.* (2004). C**60**, o44–o46