

for hollandite II. The space group was suggested as C_{2h}^5-I4/m , C_4^2-I4 , S_4^2-I4 in the tetragonal system and C_{2h}^3-I2/m , C_2^3-I2 , C_2^3-Im in the monoclinic system, but the structure was derived on the tetragonal basis.

The morphological measurements on a single crystal of hollandite (Fermor's collection No. J 941 from Kajlidongri) with a two circle goniometer give the values,

$$mm'(110 \wedge \bar{1}10) = 89^\circ 42' \pm 12'$$

and

$$ma(110 \wedge 100) = 44^\circ 36' \pm 12'.$$

The rotation and zero-layer Weissenberg photographs (Fe $K\alpha$) about [010] and [100] and equi-inclination 1st and 2nd layer Weissenberg photographs about [010] show the monoclinic symmetry of the crystal with the unit cell

$$a = 10.02, b = 5.76, c = 9.89 \text{ \AA}; \beta = 90^\circ 36'.$$

The weak odd layers in the b axis rotation photographs have also been obtained using Mo $K\alpha$ radiation. The conditions limiting possible reflexions are $h0l$ only with $h+l=2n$, and $0k0$ only with $k=2n$. This indicates the space group $P2_1/n$ (C_{2h}^5). The possibility of centering on the b face was eliminated by taking a rotation photograph about the diagonal axis [101]. The odd layer lines in the rotation photograph with [010] as axis are much weaker than the even layer lines. The cell dimension about [010] appears approximately halved, that is, the molecules repeat approximately at intervals of $b/2$ (Lipson & Cochran, 1953).

The powder spacing data of hollandite (J 941) are almost identical with those reported by Byström & Byström (1950). The indexing with the above cell dimensions is shown in Table 1. The chemical analysis of hollandite (carefully isolated well-developed crystals, J 941) by B. D. Sarma in this laboratory gives in percentage MnO₂ = 65.92, MnO = 5.44, Fe₂O₃ = 12.02, Al₂O₃ = 0.50, BaO = 16.08, H₂O = none, total = 99.96. The spectrum analysis shows traces of Si, K, Pb, Na, Mg, Ca and minute traces of Cu, Ti, Ni, Co, Bi, Sb, Li, Sn, In, Ga

and Ge. The number of atoms in the unit cell per 16 oxygen atoms comes out at Mn⁴⁺ = 6.26, Mn²⁺ = 0.63, Fe = 1.24, Ba = 0.87, Al = 0.08 and the formula may be taken as BaFeMn₇O₁₆, where Mn and Fe are present in different valency states. With the above values of axial lengths and the angle β , ($V = 571 \text{ \AA}^3$), and the density 4.92 g.cm.⁻³ for hollandite (determined for the crystal, J 941), the number of molecules per unit cell comes out to be $Z = 2.03$. The axial lengths and angle determined for a single crystal of hollandite (Museum No. K 302, collected by H. J. Winch from Kajlidongri) are

$$a = 10.03, b = 5.76, c = 9.90 \text{ \AA}; \beta = 90^\circ 42'.$$

The chemical analysis of this hollandite by Winch (1909) gives Mn⁴⁺ = 6.29, Mn²⁺ = 0.60, Fe = 1.10, Ba = 0.96, Al = 0.15 (H₂O nil). With the values of axial lengths and angle β , ($V = 572 \text{ \AA}^3$), and the density 4.94 g.cm.⁻³ (determined for the crystal, K 302) Z comes out to be 2.04.

Byström & Byström observed that all the weak reflexions in the powder photographs of Swedish hollandite II could not be indexed with the same set of crystal elements suggesting the presence of another phase of hollandite in this specimen. It is, however, found possible to index all the reflexions with the same cell reported by Byström & Byström if the b axial length is doubled.

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A preliminary crystallographic investigation of 1-phenylhydantoin and three derivatives of uracil.* By RAYMOND GERDIL, *Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.*

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A preliminary investigation has been made of the crystallographic data of 4-methyl-5-ethyluracil (I), 4-methyluracil-5-acetic acid (II), 4-methyl-5-methylamino-uracil (III), and 1-phenylhydantoin (IV). The lattice constants and space-group data were obtained from rotation and Weissenberg photographs; the determinations were made on the basis of one crystal setting for each species, and the measurements were corrected for

film shrinkage. The angular constants of the direct cells were determined by the method of angular lag (Buerger, 1942): from measurements on (1) an equi-inclination photograph of the first layer in monoclinic cases, (2) a composite anti-equi-inclination photograph (of the zero and first layers, respectively) in triclinic cases. The crystal densities were determined by flotation. The errors are estimated to be about $\pm 0.05 \text{ \AA}$ for the linear constants and about $\pm 0^\circ 20'$ for the angular constants.

(I) $\text{NHCONHC}(\text{CH}_3):\text{C}(\text{C}_2\text{H}_5)_2\text{CO}$ crystallizes in two

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different habits with two different unit cells according

Table I. *Crystallographic data*

Com- pound	Space group	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	ρ_0	<i>Z</i>	ρ_c
I	(a) <i>P</i> 1 or <i>P</i> $\bar{1}$	4.83 Å	7.45 Å	11.7 Å	92° 30'	99° 55'	108° 00'	1.30	2	1.30
	(b) <i>P</i> 1 or <i>P</i> $\bar{1}$	9.51	13.0	16.1	129° 50'	94° 55'	94° 10'	1.31	8	1.35
II	<i>P</i> 2 ₁ / <i>c</i>	4.88	12.63	12.89	—	103° 23'	—	1.57	4	1.58
III	<i>P</i> 2 ₁ / <i>c</i>	4.72	23.64	10.14	—	132° 47'	—	1.35	4	1.35
IV	<i>P</i> 1 or <i>P</i> $\bar{1}$	9.45	14.38	15.49	121° 25'	108° 10'	91° 30'	1.38	8	1.39

to the conditions of growth; both lattices are triclinic. (a) Acicular crystals were obtained from aqueous solutions evaporated at room temperature. The shortest unit translation occurs along the needle axis. (b) Well-shaped parallelepipeds were grown from concentrated aqueous solutions slowly evaporated at 50–60 °C.; the crystals were filtered from the hot mother liquor.

(II) $\text{NHCONHC}(\text{CH}_3):\text{C}(\text{CH}_2\text{COOH})\text{CO}$ recrystallizes from water in the form of prismatic needles. The shortest unit translation lies parallel to the needle axis.

(III) $\text{NHCONHC}(\text{CH}_3):\text{C}(\text{NHCH}_3)\text{CO}$ crystallizes in

the form of platy orange crystals by slow evaporation of an aqueous solution at room temperature.

(IV) $\text{N}(\text{C}_6\text{H}_5)\text{CONHCOCH}_2$ forms large bladed crystals which were easily obtained by recrystallization from water with the *a* axis chosen parallel to the main morphological axis of the crystal.

Reference

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On the arrangement of the water molecules in the crystal structure of caffeine.*

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Recently Sutor (1958) has determined the crystal structure of caffeine and refined it by the use of data of the type *hk*0 and *hk*1. A surprising result was the finding that although the *hk*0 data indicated the presence of about 80% of a water molecule of crystallization per molecule of caffeine, the *hk*1 data indicated the presence of only 40% of a water molecule. Sutor suggests that the crystals may lose water during the process of photography, but points out that she was unable to detect any change in unit-cell dimensions or density.

A further surprising result of the structure determination was the extremely—indeed, prohibitively—short distance of about 2.25 Å between adjacent sites of the water molecules, which form chains along the *c* axis. Sutor points out that if the water molecules were equally spaced along the *c* axis with only 80% of them present the OH...O distance would then be about 2.7 Å; however, such an arrangement would either lead to additional layer lines (if the spacing were coherent with respect to the repeat distance c_0) or the contribution of the water molecules to the *hk*1 data would vanish (if the spacing were incoherent or the arrangement were disordered). Furthermore, such a structure would not be consistent with the hydrogen bond between the water molecule and N₉ of the iminazole ring.

We propose an alternative arrangement for the water molecules which agrees with all evidence cited by Sutor and which is based on an analogy with the distribution

of the water molecules in the crystal structure of thymine monohydrate (Gerdil, 1960). In our proposed arrangement the water molecules form relatively short zig-zag chains with a more reasonable OH...O distance. Although within each chain the positions of the several water molecules are fixed, the overall structure can be pictured in terms of a random distribution of sites about an average position.

We first assume that all crystals of the hydrated caffeine contain approximately the same amount of water—presumably about 80% of a molecule of water per molecule of caffeine. The fact that the *hk*1 data indicate the presence of only 40% of a water molecule can then be explained in two ways: (1) the water molecules have a large anisotropic temperature factor such that $\exp(-\gamma l^2) = \exp(-\gamma) = \frac{1}{2}$; (2) the water molecules are distributed in a random fashion over a number of sites having varying *z* coordinates but with a well-defined average coordinate (z_0) of about 0.258 (Sutor, 1958). The root mean square displacement of the water molecule as implied by the anisotropic temperature factor in (1) would correspond to about 0.7 Å, clearly an improbable value if to be attributed to the actual thermal movement of a single atom. However, as pointed out in the crystal structure of thymine monohydrate (Gerdil, 1960), such an apparently high anisotropy can be simulated by a localized disorder of the type described under (2). In the case of thymine, where a similar arrangement of water molecules seems to prevail, the electron density associated with the water molecule, calculated from complete three-dimensional data, is highly elongated in the direction of the chain of water molecules and the apparent

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