

hydroxyquinoxaline where the C—C distance is 1.451 Å (Stępień, Grabowski, Cygler & Wajsman, 1976).

The molecules are linked by N—H...O hydrogen bonds. The arrangement of the molecules and hydrogen bonds is given in the projection of the structure down the *z* axis (Fig. 1). The primed molecule is linked by hydrogen bonds to two unprimed molecules, related by translation along the *z* axis: to one by a single hydrogen bond (H...O 2.42 Å), and to the other by a bifurcated hydrogen bond (H...O 2.23 and 2.40 Å). Such an arrangement forms a chain directed along the *z* axis. The unprimed molecule is linked to the centrosymmetric one by two strong hydrogen bonds (H...O 2.12 Å) joining the two chains.

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The Crystal and Molecular Structure of 5-Chloro-7-amino-2,3-dihydroxyquinoxaline Hydrochloride

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Crystals of $C_8N_3O_2H_6Cl \cdot 0.52HCl$ are orthorhombic, space group *Pbca*, with $a = 8.554$ (2), $b = 16.639$ (3), $c = 13.402$ (3) Å, $Z = 8$. 1430 independent reflexions were measured on a single-crystal diffractometer. The structure was solved by direct methods and refined by full-matrix least squares (159 parameters) to a final $R = 0.040$. The compound exists as crystals in the keto form only (the average C—O bond distance is 1.226 Å). The carbon ring is aromatic with an average C—C bond distance of 1.391 Å; the heterocyclic ring is not aromatic. The molecules are linked by strong N—H...O hydrogen bonds.

Introduction

The structures of derivatives of hydroxyquinoxaline had not been studied, in spite of their interesting features. Such studies were, therefore, started in our Department (Stępień, Grabowski, Cygler & Wajsman, 1976; Grabowski, Stępień, Cygler & Wajsman, 1977). This paper is a continuation of this work. Crystals of 5-chloro-7-amino-2,3-dihydroxyquinoxaline were obtained from the Centre for Research and Development of Dyes in Zgierz, Poland. The preparation of the pure amine is difficult; what is commonly obtained is a mixture of the amine with some of its hydrochloride. It was found in this work that the hydrochloride is joined to the amine not ionically, but by hydrogen bonds. This explains why the chemical analysis for Cl in the hydrochloride was unsatisfactory. In this investigation the fractional occupancy value of this Cl atom was refined in addition to its remaining parameters.

Experimental

The crystals used in the X-ray measurements had average dimensions of 0.3 mm. The intensities were measured on a CAD-4 diffractometer in Jagellonian University, Regional Laboratory of Physicochemical Analysis and Structure Research, by the θ - 2θ scan

Table 1. *Crystal data*

Space group <i>Pbca</i>	$D_m = 1.603 \text{ g cm}^{-3}$
$a = 8.554$ (2) Å	$D_x = 1.604$
$b = 16.639$ (3)	Systematic absences
$c = 13.402$ (3)	$hk\cdot$: $h = 2n + 1$
$V = 1907.51 \text{ Å}^3$	$h0l$: $l = 2n + 1$
$Z = 8$	$0kl$: $k = 2n + 1$
$\mu r(\text{Cu K}\alpha) = 0.71$	$h00$: $h = 2n + 1$
	$0k0$: $k = 2n + 1$
	$00l$: $l = 2n + 1$

method, up to the limit of $2\theta = 150^\circ$ (Cu $K\alpha$ radiation). 1588 independent reflexions were measured. Of these, 1430 fulfilled the condition $I > 1.96\sigma(I)$; the remaining 158 reflexions were treated as unobserved. The accurate cell constants (Table 1) were refined by the least-squares method. No absorption correction was applied and the intensities were converted to $|F|^2$ in the usual way.

Structure determination

Because of the presence of the Cl atom in the molecule, Patterson's method was applied. However, no satisfactory results were obtained. The structure was solved by the symbolic addition method. 159 reflexions with $E > 1.64$ were used. Of the three symbols used, two were given phases unequivocally. On this basis 356 reflexions with $E > 1.20$ were given phases. From the two variants of the E map, one gave approximate parameters of the atoms. The molecule of the compound investigated consists of 14 atoms, while the E

map contained 15 peaks, one of these being much higher than the others. The location of the additional high peak was in agreement with the position of the Cl atom in the hydrochloride.

The structure was refined by full-matrix least squares. In the refinement Cruickshank's weighting scheme, $w^{-1} = A + BF_o + CF_o^2$, was used with A, B, C calculated after each cycle by the method of Lee (1974). The progress of the refinement is shown in Table 2.

Table 2. Progress of the refinement

	<i>R</i>
<i>E</i> map	0.276
Four cycles of least squares with isotropic temperature factors	0.126
Four cycles with anisotropic temperature factors	0.052
Three cycles including hydrogen atoms	0.040

Table 3. The fractional coordinates ($\times 10^4$) with standard deviations resulting from least-squares refinement

	<i>x</i>	<i>y</i>	<i>z</i>
Cl(1)	-24696 (8)	6841 (4)	32461 (6)
O(1)	4574 (2)	1043 (1)	4964 (2)
O(2)	2377 (2)	2130 (1)	4397 (2)
N(1)	3046 (3)	33 (1)	4380 (2)
N(2)	747 (3)	1118 (1)	3950 (2)
N(3)	-318 (3)	-2179 (1)	3409 (2)
C(1)	3354 (3)	804 (1)	4573 (2)
C(2)	2117 (3)	1415 (1)	4292 (2)
C(3)	-978 (3)	10 (1)	3474 (2)
C(4)	-1237 (3)	-801 (2)	3343 (2)
C(5)	-51 (3)	-1355 (1)	3559 (2)
C(6)	1383 (3)	-1074 (2)	3898 (2)
C(7)	1620 (3)	-256 (2)	4020 (2)
C(8)	453 (3)	304 (1)	3815 (2)
H(1)	3747 (47)	-298 (24)	4540 (28)
H(2)	-29 (48)	1466 (23)	3777 (28)
H(3)	-2233 (45)	-970 (25)	3125 (29)
H(4)	2220 (45)	-1421 (23)	4037 (28)
H(5)	378 (47)	-2504 (24)	3804 (29)
H(6)	-136 (48)	-2204 (25)	2932 (33)
Cl(2)	3904 (3)	2548 (1)	1443 (2)
H(7)	4764 (99)	2728 (48)	2096 (63)

Table 4. Distances (Å) and angles ($^\circ$) with estimated standard deviations

Intramolecular distances and angles

C(1)—O(1)	1.234 (3)	C(3)—C(4)	1.378 (4)
C(2)—O(2)	1.219 (3)	C(3)—C(8)	1.395 (3)
C(1)—N(1)	1.335 (3)	C(4)—C(5)	1.402 (4)
C(2)—N(2)	1.352 (3)	C(5)—C(6)	1.389 (4)
C(1)—C(2)	1.515 (4)	C(6)—C(7)	1.386 (4)
C(7)—N(1)	1.397 (3)	C(7)—C(8)	1.393 (3)
C(8)—N(2)	1.390 (3)	C(3)—Cl(1)	1.727 (3)
		C(5)—N(3)	1.404 (4)
N(1)—H(1)	0.84 (4)	N(3)—H(5)	0.96 (4)
N(2)—H(2)	0.91 (4)	N(3)—H(6)	0.66 (4)
C(4)—H(3)	0.94 (4)	Cl(2)—H(7)	1.18 (8)
C(6)—H(4)	0.94 (4)		

C—C (mean) in aromatic ring 1.391 (3)

O(1)—C(1)—N(1)	124.0 (2)	C(4)—C(5)—C(6)	119.1 (2)
O(1)—C(1)—C(2)	118.7 (2)	C(4)—C(5)—N(3)	119.7 (2)
N(1)—C(1)—C(2)	117.3 (2)	N(3)—C(5)—C(6)	121.2 (2)
O(2)—C(2)—N(2)	123.7 (2)	C(5)—C(6)—C(7)	119.9 (2)
O(2)—C(2)—C(1)	119.9 (2)	N(1)—C(7)—C(6)	120.5 (2)
N(2)—C(2)—C(1)	116.4 (2)	N(1)—C(7)—C(8)	117.6 (2)
C(1)—N(1)—C(7)	124.8 (2)	C(6)—C(7)—C(8)	121.9 (2)
C(2)—N(2)—C(8)	123.9 (2)	N(2)—C(8)—C(3)	122.9 (2)
Cl(1)—C(3)—C(4)	119.6 (2)	N(2)—C(8)—C(7)	119.8 (2)
Cl(1)—C(3)—C(8)	118.6 (2)	C(3)—C(8)—C(7)	117.3 (2)
C(4)—C(3)—C(8)	121.8 (2)	C(3)—C(4)—C(5)	120.0 (2)
H(1)—N(1)—C(1)	116 (2)	H(4)—C(6)—C(5)	122 (2)
H(1)—N(1)—C(7)	119 (2)	H(4)—C(6)—C(7)	118 (2)
H(2)—N(2)—C(2)	119 (2)	H(5)—N(3)—C(5)	112 (2)
H(2)—N(2)—C(8)	117 (2)	H(6)—N(3)—C(5)	99 (4)
H(3)—C(4)—C(3)	118 (3)	H(5)—N(3)—H(6)	110 (4)
H(3)—C(4)—C(5)	121 (3)		

Intermolecular distances and angles

Symmetry code

(i)	$1 - x,$	$-y,$	$1 - z$
(ii)	$x - \frac{1}{2},$	$y,$	$\frac{1}{2} - z$
(iii)	$\frac{1}{2} - x,$	$y - \frac{1}{2},$	z
(iv)	$-x,$	$y - \frac{1}{2},$	$\frac{1}{2} - z$
N(1)—O(1) ^j	2.850 (3)	N(1)—H(1)—O(1) ^j	175 (4)
H(1)—O(1) ^j	2.01 (4)	N(2)—H(2)—Cl(2) ⁱⁱ	158 (4)
N(2)—Cl(2) ⁱⁱ	2.904 (3)	N(3)—H(5)—O(2) ⁱⁱⁱ	155 (3)
H(2)—Cl(2) ⁱⁱ	2.04 (4)	N(3)—H(6)—Cl(2) ⁱⁱⁱ	164 (4)
N(3)—O(2) ⁱⁱⁱ	3.066 (4)	N(3)—H(7) ^{iv} —Cl(2) ^{iv}	154 (7)
H(5)—O(2) ⁱⁱⁱ	2.16 (4)		
N(3)—Cl(2) ⁱⁱⁱ	2.935 (4)		
H(6)—Cl(2) ⁱⁱⁱ	2.29 (4)		
Cl(2) ^{iv} —N(3)	3.107 (4)		
H(7) ^{iv} —N(3)	1.83 (8)		

At this stage a difference synthesis was calculated which revealed all H atom positions – in the 5-chloro-7-amino-2,3-dihydroxyquinoxaline molecule as well as in the hydrochloride. The final cycles of refinement were performed with anisotropic thermal parameters for the non-hydrogen atoms, and positional parameters for the H atoms. The individual isotropic thermal parameters for the H atoms were assumed to be the same as the average anisotropic parameters of the atom to which they are attached.

The final parameters are listed in Table 3 together with the standard deviations. The interatomic distances and bond angles are listed in Table 4 (the values have not been corrected for thermal motion). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).*

Description of the structure

The carbon and heterocyclic rings of the molecule are planar but make an angle of 1.6° with each other. The deviations from the 'best' planes given by the equations $-2.78350x - 1.11019y + 12.64101z = 4.66157$ for the carbon ring and $-3.00133x - 1.23598y + 12.51041z = 4.58147$ for the heterocyclic ring are listed in Table 5 (x , y and z are the parameters of the atoms). O(1) is out of the plane by as much as 0.127 \AA , and forms the C–O bond which is 0.014 \AA longer than the other. This is caused by strong N–H...O hydrogen-bond formation (N–O 2.850 \AA , H...O 2.01 \AA). The mean C–O bond length (1.226 \AA) indicates typical double-bond character and the keto form of the compound in the crystalline state. The planarity of the carbon ring and also the C–C distances show an aromatic character for that ring. The mean C–C distance in this configuration is 1.515 \AA . This exceeds the mean distance in typical conjugated double-bond systems (e.g. butadiene 1.461 \AA). The elongation of the

bond is due to the presence of fractional charges on both the C(carbonyl) atoms – as in oxalic acid (1.538 \AA , Delaplane & Ibers, 1969). In 5-chloro-7-nitro-2,3-dihydroxyquinoxaline the analogous bond distance is 1.511 \AA (Grabowski, Stępień, Cygler & Wajsman, 1977). If one of the electronegative O atoms in such a system is replaced by a neutral atom, the elongation of the bond does not take place, e.g. 2-hydroxyquinoxaline where the C–C distance is 1.451 \AA (Stępień, Grabowski, Cygler & Wajsman, 1976).

During the refinement it became apparent that there is a fractional occupancy factor for the hydrochloride molecule. The final value (after refinement) is 0.52 . The Cl–H distance in the hydrochloride molecule is $1.18(8) \text{ \AA}$. A three-dimensional system of hydrogen bonds exists in this structure. Each pair of centrosymmetric molecules is linked by two strong N–H...O bonds (H...O 2.01 \AA). The second O atom forms a weaker hydrogen bond with the amine group of the neighbouring pair (N–H and H...O are 2.066 and 2.16 \AA respectively). Each centrosymmetric pair of molecules is joined to four others. Hence, a layer of molecules, parallel to the (001) plane, is formed. The statistically distributed hydrochloride molecules are linked to the 5-chloro-7-amino-2,3-dihydroxyquinoxaline molecules, which enclose them, through three hydrogen bonds: two to amine groups of neighbouring layers (Cl–H...N with H...N 1.83 \AA , and Cl...H–N with Cl...H 2.29 \AA) and the third to the N atom of the heterocyclic ring of another molecule (Cl...H 2.04 \AA). Thus, they join the layers into a three-dimensional net.

The numbering of the atoms, the arrangement of the molecules and the hydrogen bonds are given in the projection of the structure down the x axis (Fig. 1).

I wish to thank the Polish Academy of Sciences for financial support.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32592 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. Deviations from the best planes (\AA)

Carbon ring		Heterocyclic ring	
C(3)	0.002	N(1)	-0.021
C(4)	-0.003	N(2)	-0.002
C(5)	0.002	C(1)	0.033
C(6)	0.000	C(2)	-0.022
C(7)	-0.002	C(7)	-0.006
C(8)	0.001	C(8)	0.017
Cl(1)	0.053	O(1)	0.127
N(3)	-0.021	O(2)	-0.054
H(3)	-0.02	H(1)	0.01
H(4)	0.02	H(2)	-0.03

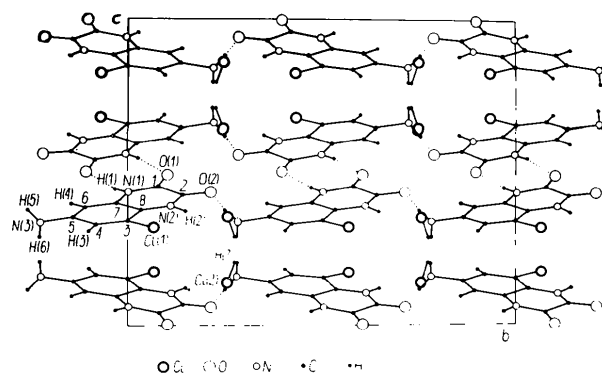


Fig. 1. The projection of the structure down the x axis. The hydrogen bonds are marked by dotted lines.

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Hydrogen Bond Studies.

CXX.* An X-ray Determination of the Crystal Structure of $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$

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The crystal structure of lithium nitrate trihydrate, $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, has been determined by X-ray diffraction at 295 K. The crystal is orthorhombic, space group *Cmcm*, $a = 6.8018$ (4), $b = 12.7132$ (9), $c = 5.9990$ (4) Å, $V = 518.75$ Å³, $Z = 4$. The nitrate ions, Li^+ ions and one of the two crystallographically non-equivalent water molecules lie in a mirror plane and are bonded to atoms in adjacent planes through the second water molecule. The Li^+ ion is octahedrally surrounded by six O atoms, four belonging to water molecules and two to nitrate ions. The two non-equivalent water molecules are present in the structure in distinctly different bonding situations. One is bonded to two Li^+ ions and is the donor of two hydrogen bonds. The other is involved in six hydrogen bonds: the O atom accepts two hydrogen bonds, and both protons are involved in bifurcated hydrogen bonds.

Introduction

This work is part of a project to determine the experimental electron density in simple solid hydrates containing only light atoms. By selecting compounds containing water molecules in a variety of different environments, it should be possible to observe, in a systematic way, the influence of the environment on the electron density of the water molecule. $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, having a high valence-electron/core-electron ratio, would seem a singularly suitable compound for this purpose. Since its crystal structure was unknown, however, an X-ray structure determination was an essential first step.

Experimental

Crystals of $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ were grown by slow evaporation at room temperature from an aqueous solution of lithium nitrate. They were highly sensitive both to humidity (deliquescent and hygroscopic) and heat (m.p. 29.9°C) (see Donnan & Burt, 1903), and

had, therefore, to be handled with extreme caution. An approximately spherical crystal of mean radius 0.058 mm was selected for the subsequent data collection and sealed in a thin-walled glass capillary. Its general quality was checked with Laue and Weissenberg photographs. In agreement with the previous findings of Aravamudan & Ramaseshan (1961), the diffraction symmetry and systematic absences in the Weissenberg photographs indicated three space-group possibilities: (a) *Cmcm* (No. 63, centrosymmetric), (b) *Cmc*₂ (No. 36, noncentrosymmetric) and (c) *C2cm* (equivalent to *Ama*₂, No. 40, noncentrosymmetric). (Space-group numbering follows that given in *International Tables for X-ray Crystallography*, 1969.)

The unit-cell dimensions were determined by powder

Table 1. *Crystal data for* $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$

FW	123.00	$\rho_{\text{calc.}}$	1.575 g cm ⁻³
Space group	<i>Cmcm</i>	$\rho_{\text{obs.}}$ *	1.55
<i>a</i>	6.8018 (4) Å	<i>Z</i>	4
<i>b</i>	12.7132 (9)	m.p.	29.9°C
<i>c</i>	5.9990 (4)	$\mu_{\text{calc.}}$	1.60 cm ⁻¹
<i>V</i>	518.75 Å ³		

* Part CXIX: Berglund & Tegenfeldt (1977).

* Aravamudan & Ramaseshan (1961).