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## Neutron Diffraction Study of L-Histidine Hydrochloride Monohydrate

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The structure of L-histidine hydrochloride monohydrate has been redetermined by neutron diffraction. 1489 symmetry-independent reflexions have been measured at  $\lambda = 1.096 \text{ \AA}$  on a four-circle neutron diffractometer. The structure has been refined to a conventional  $R(F^2) = 0.036$  including a treatment for anisotropic extinction. Further data for 183 independent reflexions on a much smaller crystal gave  $R(F^2) = 0.026$  by refining scale and extinction factors only. The positions of the heavy atoms are in agreement with a previous X-ray study. The positions of the H atoms have been determined and the hydrogen-bonding scheme is discussed. The histidine molecule adopts the closed form with a planar imidazole group folded back on a planar carboxyl group.

### Introduction

Several compounds related structurally to the amino acid histidine have been studied by neutron diffraction. L-Histidine in the orthorhombic modification was reported by Lehmann, Koetzle & Hamilton (1972). The metal–histidine complex bis(L-histidinato)cadmium dihydrate is described by Fuess & Bartunik (1976). The X-ray structure of the orthorhombic form of L-histidine is given by Madden, McGandy & Seeman (1972), that of the monoclinic form by Madden, McGandy, Seeman, Harding & Hoy (1972). The hydrochloride was studied for DL-histidine by Bennett, Davidson, Harding & Morelle (1970) and for L-histidine by Donohue, Lavine & Rollett (1956) and Donohue & Caron (1964) (referred to as DC). The conformation of the histidine molecule in different structures has been discussed by Kistenmacher, Hunt & Marsh (1972) who studied L-N-acetylhistidine monohydrate.

Our present study was begun with two aims: one was a comparison of histidine as the hydrochloride with the conformation as a molecule and in metal–histidine complexes, the other was an evaluation of the modified Laue film technique in neutron diffraction and an estimation of the precision at present available by neutron film techniques. We therefore collected a full data set by the modified Laue technique (Hohlwein, 1975), which was refined in parallel with the data set from the conventional four-circle neutron instrument. The crystal used for the film study had a volume of only  $0.3 \text{ mm}^3$ . A full account of this work will be given elsewhere (Hohlwein & Fuess, 1977). In the present paper we shall describe the structure refinement from four-circle data: a complete set from a  $4.3 \text{ mm}^3$  crystal and a limited set from the  $0.3 \text{ mm}^3$  crystal.

### Experimental

The crystals were prepared as a by-product when we tried to prepare rare-earth–histidine crystals intended

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Table 1. *Crystal data for L-histidine hydrochloride monohydrate*

$a$	= 15.36 Å	$C_6O_2N_3H_9 \cdot HCl \cdot H_2O$
$b$	= 8.92	Space group $P2_12_12_1$
$c$	= 6.88	$Z = 4$
$V$	= 942.6 Å <sup>3</sup>	$\mu = 2.04 \text{ cm}^{-1}$ (calculated)
$\lambda$	= 1.096 Å	$\mu = 2.8$ (measured for $\lambda = 1.5 \text{ Å}$ )

for the study of anomalous dispersion methods in neutron diffraction.  $Sm_2(CO_3)_3$  was dissolved in a boiling saturated solution of L-histidine in water, and a few drops of 0.1 M HCl were added to obtain a clear solution. Well shaped, colourless crystals were obtained by slow evaporation. X-ray fluorescence showed the total absence of Sm. Microanalysis and X-ray photographs confirmed the composition and the unit cell of L-histidine hydrochloride monohydrate. Crystal data are summarized in Table 1.

A small crystal  $0.7 \times 0.7 \times 0.6$  mm (crystal 1 in the following) was chosen for the modified Laue measurements. About 350 (183 symmetry-independent) reflexions were measured from the same crystal on the D8 four-circle instrument at the HFR at ILL, Grenoble. A second crystal (crystal 2) about  $1 \times 2 \times 2$  mm along **a**, **b** and **c**, with a volume of 4.3 mm<sup>3</sup>, was selected for full data collection on the same facility. The wavelength from the (200) planes of a Cu monochromator was  $\lambda = 1.096 \text{ Å}$  giving a flux of about  $2 \times 10^7 \text{ n cm}^{-2} \text{ s}^{-1}$  at the sample position. Data were collected in the  $\theta$ - $2\theta$  step-scan mode at a rate of about 8 min per reflexion.

The step size was varied as a function of  $\theta$  in order to obtain a fixed number of points in the peak. The detector aperture was made large enough to accept virtually all Bragg intensity. 1489 independent reflexions were measured up to a maximum  $2\theta = 95^\circ$ ; of these 66 had  $I < \sigma(I)$ .

Background corrections were applied (Lehmann & Larsen, 1974). Data were corrected for absorption by a Gaussian grid method with *ABSORB* (X-RAY system, 1972). Assuming an incoherent cross-section for H of  $\sigma_{\text{inc}} = 40$  barns at  $\lambda = 1.0 \text{ Å}$ , the absorption coefficient has been calculated to be  $\mu = 2.04 \text{ cm}^{-1}$ . Transmission coefficients were between 0.75 and 0.85 for crystal 2 and 0.90 and 0.96 for crystal 1. No correction for thermal diffuse scattering was made.

### Structure refinement

The refinement was carried out on the complete data set of crystal 2 with *ORXFLS3* (Busing *et al.*, 1972). The starting parameters were the atomic positions given by DC together with isotropic temperature factors. The weights were  $w = 1/\sigma(F_o^2)$  with  $\sigma(F_o^2) = [\sigma_o^2(F_o^2) + (0.03F_o^2)^2]^{1/2}$ , where  $\sigma(F_o^2)$  is based on

counting statistics. The quantity minimized was  $\sum w(F_o^2 - F_c^2)^2$ . The values for the scattering lengths are:  $b_O = 0.5804$ ,  $b_C = 0.6648$ ,  $b_N = 0.937$ ,  $b_H = -0.3741$ ,  $b_{Cl} = 0.9579$  (all in  $10^{-12} \text{ cm}$ ; Koester, 1975). With the initial parameter set, the refinement stopped at  $R = 20\%$  due to a misplaced H atom of the water molecule H(12). The  $x$  parameter of this atom was given by DC as 0.223. A new value for this parameter was easily found from a difference synthesis and the refinement then converged rapidly with anisotropic temperature factors for all atoms. An isotropic extinction parameter was included at a late stage of the refinement. An anisotropic extinction correction of type II (Coppens & Hamilton, 1970) was taken into account for the last two cycles. The shift in the positional and thermal parameters due to this treatment was less than one standard deviation in all cases.  $R(F^2) = |\Sigma(F_o^2 - F_c^2)^2 / \Sigma F_o^4|^{1/2}$  dropped from 0.044 to 0.038. The  $R$  factor ratio test (Hamilton, 1972) on the weighted  $R$  values shows that this improvement has a 99% significance. The values for the anisotropic extinction parameters are given in Table 2 for both crystals, together with the isotropic extinction parameter  $g$ . The  $g$  value is a parameter in a Gaussian mosaic angle distribution. The anisotropic  $w_{ij}$ 's are elements of a tensor describing the particle size as an ellipsoid. An attempt to refine the data by an anisotropic extinction of type I (extinction dominated by mosaic spread) did not improve the residual compared to the isotropic treatment. It seems, therefore, that in these crystals extinction is governed essentially by particle-size effects.

The 183 symmetry-independent reflexions of crystal 1 were treated in the following way. Positional and thermal parameters for all atoms were taken as obtained for crystal 2, then one cycle of refinement was carried out for the scale factors and two cycles for scale and extinction factors. The  $R$  values for the final stages are given in Table 2.\*

## Results and discussion

### Bond distances and conformation

The atomic coordinates and thermal parameters are given in Table 3, the distances and angles in Table 4. The molecule is shown in Fig. 1. The histidine molecule consists of two groups of very nearly coplanar atoms (Table 5). The two groups are turned towards each other and the molecule is said to exist in the closed form (Kistenmacher *et al.*, 1972). This conformation is

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32082 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

found if the torsion angle about C(1)–C(2)–C(3)–C(4), which links the two planar groups, has a value of about  $-50^\circ$ . The closed form is observed in all metal–histidine complexes (e.g. Cd–histidine) and in L-histidine hydrochloride.

Histidine itself (in the two possible modifications) and DL-histidine hydrochloride adopt the open form, which is present when the above-mentioned torsion angle is near  $180^\circ$ . The torsion angles of the title compound are compared in Table 6 with the same values in related structures. The distances between C and N atoms (in the imidazole ring and for the amide group) in several histidine compounds are given in Table 7. There are no significant variations between the X-ray and neutron results, nor among histidine, histidine hydrochloride and metal–histidine complexes.

### Hydrogen bonding

The crystal structure and the hydrogen bonds are shown in Fig. 2. Two pairs of imidazole rings are

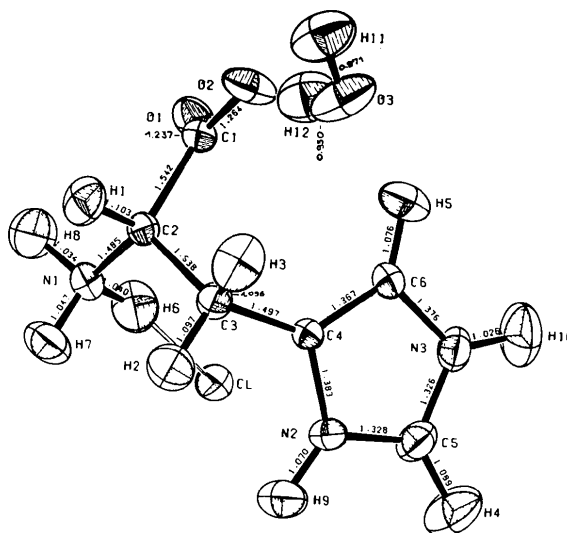


Fig. 1. The molecular structure of L-histidine hydrochloride monohydrate. The thermal ellipsoids are at the 50% probability level.

Table 2. *R* values and extinction parameters for the two crystals

Extinction type	Crystal volume (mm <sup>3</sup> )	<i>g</i>	<i>W</i> <sub>11</sub>	<i>W</i> <sub>22</sub>	<i>W</i> <sub>33</sub>	<i>W</i> <sub>12</sub>	<i>W</i> <sub>13</sub>	<i>W</i> <sub>23</sub>	<i>R</i> ( <i>F</i> )	<i>R</i> ( <i>F</i> <sup>2</sup> )	<i>R<sub>w</sub></i> ( <i>F</i> <sup>2</sup> )	Scale	Number of reflexions
Isotropic	{4.3	1.14							0.039	0.044	0.055	6.91	1489
	{0.3	0.51							0.024	0.035	0.045	2.09	183
Anisotropic (type II)	{4.3		2.24	0.58	0.41	-0.02	0.08	0.16	0.038	0.038	0.053	6.88	1489
	{0.3		7.32	10.03	7.94	6.04	6.06	8.87	0.021	0.026	0.041	2.09	183

Table 3. Fractional coordinates ( $\times 10^4$ ) and temperature parameters ( $\times 10^4$ )

The temperature parameters are given as  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}2hk + \dots)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	3643 (1)	1934 (1)	5064 (2)	22 (1)	53 (1)	75 (2)	1 (1)	4 (1)	3 (1)
C(2)	4013 (1)	1163 (1)	3236 (2)	17 (1)	45 (1)	80 (2)	5 (1)	3 (1)	-1 (1)
C(3)	4510 (1)	2240 (1)	1888 (2)	19 (1)	54 (1)	100 (2)	3 (1)	9 (1)	2 (1)
C(4)	4012 (1)	3613 (1)	1311 (2)	20 (1)	43 (1)	73 (2)	-2 (1)	5 (1)	-3 (1)
C(5)	3403 (1)	5253 (2)	-1988 (2)	32 (1)	72 (2)	127 (3)	-2 (1)	-11 (1)	27 (2)
C(6)	3678 (1)	4758 (1)	2403 (2)	28 (1)	47 (1)	93 (2)	1 (1)	6 (1)	-8 (1)
N(1)	3306 (1)	374 (1)	2176 (1)	23 (1)	51 (1)	102 (2)	-1 (1)	-1 (1)	-11 (1)
N(2)	3833 (1)	3962 (1)	-606 (1)	29 (1)	65 (1)	77 (2)	-5 (1)	1 (1)	3 (1)
N(3)	3301 (1)	5754 (1)	1130 (2)	31 (1)	49 (1)	151 (2)	4 (1)	3 (1)	9 (1)
O(1)	2854 (1)	1840 (2)	5398 (2)	23 (1)	78 (2)	137 (3)	1 (1)	18 (1)	-23 (2)
O(2)	4202 (1)	2635 (2)	6061 (2)	32 (1)	132 (3)	97 (3)	-18 (1)	3 (1)	39 (2)
O(3)	5813 (1)	4011 (3)	5867 (3)	33 (1)	182 (4)	175 (5)	19 (1)	8 (2)	89 (4)
Cl	1757 (1)	2275 (1)	306 (1)	32 (1)	62 (1)	98 (2)	7 (1)	-2 (1)	1 (1)
H(1)	4473 (2)	293 (3)	3732 (4)	31 (1)	81 (3)	181 (6)	15 (2)	-8 (2)	19 (4)
H(2)	4710 (2)	1638 (3)	573 (5)	55 (2)	101 (4)	162 (6)	17 (2)	43 (3)	-7 (4)
H(3)	5108 (2)	2569 (4)	2645 (5)	24 (1)	120 (4)	258 (8)	-5 (2)	-12 (3)	33 (5)
H(4)	3194 (3)	5826 (4)	-1889 (5)	62 (2)	141 (5)	196 (7)	11 (3)	-32 (3)	65 (5)
H(5)	3682 (3)	4960 (4)	3945 (4)	63 (2)	117 (4)	111 (5)	14 (2)	4 (3)	-31 (4)
H(6)	2808 (2)	1083 (3)	1724 (5)	31 (1)	95 (3)	201 (7)	3 (2)	-17 (2)	-8 (4)
H(7)	3558 (2)	-177 (3)	956 (4)	40 (1)	97 (3)	133 (5)	4 (2)	4 (2)	-38 (4)
H(8)	3046 (2)	-443 (3)	3070 (5)	40 (1)	103 (4)	193 (7)	-20 (2)	6 (3)	7 (4)
H(9)	3975 (2)	3326 (3)	-671 (4)	45 (1)	110 (4)	107 (5)	-9 (2)	4 (2)	-3 (4)
H(10)	2965 (2)	6716 (3)	1453 (6)	47 (1)	79 (3)	312 (10)	18 (2)	22 (3)	-2 (5)
H(11)	6113 (2)	3689 (5)	7067 (6)	47 (2)	180 (5)	193 (7)	12 (3)	19 (3)	52 (6)
H(12)	5270 (2)	3500 (4)	5889 (5)	38 (1)	165 (5)	193 (7)	11 (2)	-1 (3)	22 (5)

Table 4. Distances (Å) and angles (°) within the molecule

C(1)—O(1)	1.237 (3)	N(1)—H(6)	1.040 (3)
C(1)—O(2)	1.264 (3)	N(1)—H(7)	1.047 (4)
C(1)—C(2)	1.542 (4)	N(1)—H(8)	1.034 (4)
C(2)—N(1)	1.485 (2)	C(3)—H(2)	1.097 (4)
C(2)—C(3)	1.538 (3)	C(3)—H(3)	1.096 (4)
C(3)—C(4)	1.497 (3)	C(5)—H(4)	1.089 (5)
C(4)—N(2)	1.383 (4)	N(3)—H(10)	1.026 (4)
N(2)—C(5)	1.328 (3)	C(6)—H(5)	1.076 (4)
C(5)—N(3)	1.326 (4)	N(2)—H(9)	1.070 (4)
N(3)—C(6)	1.376 (3)	O(3)—H(11)	0.971 (5)
C(6)—C(4)	1.368 (3)	O(3)—H(12)	0.950 (4)
C(2)—H(1)	1.103 (3)		
O(1)—C(1)—O(2)	126.7 (2)	C(2)—C(3)—H(3)	107.3 (2)
O(1)—C(1)—C(2)	118.9 (1)	C(4)—C(3)—H(2)	108.9 (2)
O(2)—C(1)—C(2)	114.4 (2)	C(4)—C(3)—H(3)	109.5 (2)
C(1)—C(2)—H(1)	107.3 (2)	H(2)—C(2)—H(3)	106.8 (3)
C(1)—C(2)—N(1)	110.0 (1)	C(3)—C(4)—N(2)	122.6 (1)
C(1)—C(2)—C(3)	113.3 (2)	C(3)—C(4)—C(6)	131.0 (2)
H(1)—C(2)—N(1)	106.7 (2)	C(4)—N(2)—C(5)	109.0 (1)
H(1)—C(2)—C(3)	108.0 (2)	N(2)—C(5)—N(3)	108.7 (1)
N(1)—C(2)—C(3)	111.3 (2)	C(5)—N(3)—C(6)	109.1 (2)
C(2)—N(1)—H(6)	113.4 (2)	N(3)—C(6)—C(4)	106.9 (2)
C(2)—N(1)—H(7)	110.2 (2)	N(2)—C(5)—H(4)	125.6 (2)
C(2)—N(1)—H(8)	109.0 (2)	N(3)—C(5)—H(4)	125.7 (3)
H(6)—N(1)—H(7)	108.5 (3)	C(5)—N(3)—H(10)	123.0 (3)
H(6)—N(1)—H(8)	108.7 (3)	C(6)—N(3)—H(10)	127.9 (3)
H(7)—N(1)—H(8)	106.8 (3)	N(3)—C(6)—H(5)	121.5 (2)
C(2)—C(3)—C(4)	114.7 (1)	C(4)—C(6)—H(5)	131.7 (2)
C(2)—C(3)—H(2)	109.3 (2)	H(11)—O(3)—H(12)	106.3 (4)

parallel to each other in the unit cell. The molecules are linked together by a hydrogen-bonding scheme *via* the water molecules and the Cl atoms (Table 8). Five H atoms of the histidine and the two of the water are available for hydrogen-bond formation. The strong intermolecular bond between N(2)—H(9) and the carboxyl group of a neighbouring molecule is the essential link between the molecules, giving rise to a spiral arrangement along *c*. The strength of this bond is illustrated by the unusually long N(2)—H(9) distance (1.070 Å). The ammonium-group H atoms form links to the O of the water molecule and to two different Cl

Table 5. Atom deviations from the least-squares planes (Å)

C(3)	0.008 (7)	C(1)	-0.006 (4)
C(4)	-0.013 (7)	C(2)	0.002 (4)
N(2)	-0.003 (7)	O(1)	0.002 (4)
C(5)	-0.001 (7)	O(2)	0.002 (4)
N(3)	0.003 (7)		
C(6)	0.004 (7)	*N(1)	-0.011
		*H(4)	-0.034
		*H(9)	0.044
		*H(10)	-0.030
		*H(5)	0.020

\* Atom not included in least-squares calculation.

Table 6. Torsion angles for some histidine compounds (°)

	L-Histidine HCl <sup>(a)</sup>	L-Histidine <sup>(b)</sup> P2 <sub>1</sub> 2 <sub>1</sub>	Cd. histidine 2H <sub>2</sub> O <sup>(c)</sup>	DL-Histidine HCl <sup>(d)</sup>
C(1)—C(2)—C(3)—C(4)	-53.0	181.4	-42.9	150.8
C(2)—C(3)—C(4)—C(5)	61.6	-123.2	125.2	114.1
C(2)—C(3)—C(4)—N(2)	-120.8	56.8	-55.2	-68.1
C(3)—C(2)—C(1)—O(1)	124.8	94.4	98.2	112.9
C(3)—C(2)—C(1)—O(2)	-54.8	83.8	-79.9	66.7
N(1)—C(2)—C(1)—O(1)	-0.5	-26.8	-23.8	-9.7
N(1)—C(2)—C(1)—O(2)	-179.3	155.1	158.1	170.7
C(1)—C(2)—N(1)—H(6)	59.8	45.8	-63.1	
C(1)—C(2)—N(1)—H(7)	-178.4	163.5	179.6	
C(1)—C(2)—N(1)—H(8)	-61.5	-76.4		

(a) Present work. (b) Madden *et al.*, 1972; Lehmann *et al.*, 1972. (c) Fuess & Bartunik, 1976. (d) Bennett *et al.*, 1970.

Table 7. Distances within the imidazole ring, and C—N distances (Å)

	L-Histidine HCl <sup>(a)</sup>	L-Histidine HCl <sup>(b)</sup>	DL-Histidine HCl <sup>(c)</sup>	L-Histidine <sup>(d)</sup>	L-Histidine <sup>(e)</sup> P2 <sub>1</sub>	L-Histidine <sup>(e)</sup> P2 <sub>1</sub> 2 <sub>1</sub>	Cd histidine <sup>(f)</sup>	Ni histidine <sup>(g)</sup>
C(3)—C(4)	1.497	1.508	1.503	1.502	1.496	1.505	1.492	1.473
C(4)—N(2)	1.383	1.386	1.385	1.376	1.392	1.382	1.384	1.393
N(2)—C(5)	1.328	1.319	1.314	1.309	1.343	1.327	1.323	1.329
C(5)—N(3)	1.326	1.314	1.359	1.349	1.335	1.339	1.339	1.338
N(3)—C(6)	1.376	1.359	1.374	1.376	1.379	1.374	1.367	1.360
C(6)—C(4)	1.368	1.358	1.374	1.372	1.389	1.361	1.361	1.379
C(2)—N(1)	1.485	1.495	1.482	1.499	1.479	1.483	1.471	1.475

(a) Present work. (b) Donohue & Caron, 1964. (c) Bennett *et al.*, 1970. (d) Lehmann *et al.*, 1972. (e) Madden *et al.*, 1972. (f) Fuess & Bartunik, 1976. (g) Fraser & Harding, 1967.

\* Neutron work.

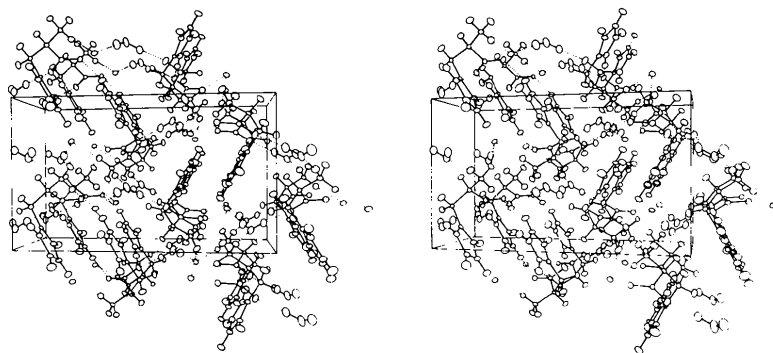


Fig. 2. Stereoscopic view of the molecular packing. The unit cell is outlined. The broken lines are hydrogen bonds.

Table 8. *Hydrogen-bond distances (Å) and angles (°)*

<i>A</i> — <i>H</i>	<i>B</i> — <i>C</i>	<i>A</i> ... <i>B</i>	<i>H</i> ... <i>B</i>	<i>A</i> — <i>H</i> ... <i>B</i>	<i>C</i> — <i>B</i> ... <i>H</i>
N(1)—H(7)	O(3)′	2.790 (5)	1.757 (5)	168.3 (3)	
O(3)′—H(11)′	Cl	3.200 (7)	2.232 (6)	174.4	
O(3)—H(12)	O(2)—C(1)	2.764 (4)	1.817 (5)	174.6 (4)	141.9 (2)
N(1)—H(6)	Cl	3.193 (4)	2.166 (4)	169.0 (3)	
N(1)—H(8)	Cl′	3.198 (6)	2.265 (5)	149.4 (3)	
N(2)′	O(2)—C(1)	2.642 (6)	1.580 (5)	170.9 (3)	121.9 (2)
N(3)—H(10)	O(1)′—C(2)′	2.829 (4)	1.941 (4)	143.1 (4)	131.3 (2)

Positions of primed atoms

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
O(1)′	0.2146	0.8160	0.0398	H(11)′	0.1113	0.1311	0.2933
Cl′	0.3243	−0.2275	0.5306	H(9)′	0.3975	0.3326	0.8114
O(3)′	0.4187	−0.0989	−0.0897				

atoms. Each Cl is stabilized in its position by links to a water H and two ammonium H's of different molecules. The second H of the water molecule forms a hydrogen bond to O(2) of the carboxyl group.

### Conclusion

It was shown that data from a small crystal of about 0.3 mm<sup>3</sup> can be collected with reasonable speed (~120 a day) with present automatic neutron equipment. The structure analysis corrected the H positions of the X-ray structure and revealed the hydrogen-bonding scheme. The precision of the data will be compared to neutron film data.

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## Influence of the Alkaline Cation on the Structures of Polymeric *o*-Phthalatocuprate(II). I. The Crystal Structures of Dilithium *catena*-Di- $\mu$ -(*o*-phthalato)-cuprate(II) Tetrahydrate and Dirubidium *catena*-Di- $\mu$ -(*o*-phthalato)-cuprate(II) Dihydrate

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(I)  $\text{Li}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ : triclinic  $P\bar{1}$ ;  $a = 7.823(7)$ ,  $b = 10.935(15)$ ,  $c = 6.514(10)$  Å,  $\alpha = 111.8(1)$ ,  $\beta = 112.8(1)$ ,  $\gamma = 87.4(1)^\circ$ ,  $Z = 1$ . (II)  $\text{Rb}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ : monoclinic  $C2/c$ ;  $a = 21.919(15)$ ,  $b = 7.827(7)$ ,  $c = 11.191(10)$  Å,  $\beta = 101.8(3)^\circ$ ,  $Z = 4$ . The structures, determined from diffractometer data by Patterson and Fourier methods, were refined by block-diagonal least squares to  $R = 2.4\%$  for (I) and  $6.6\%$  for (II). In both compounds Cu is square-planar, coordinated by four O atoms from four phthalate groups. The phthalate anions bridge adjacent Cu atoms in polymeric chains, which are linear in (I) and zigzag in (II). Coordination of Li is tetrahedral and involves two O atoms from two phthalate groups, belonging to the same chain, and two water molecules. A different behaviour is found for Rb which interposes between two different chains and is surrounded by eight O atoms from four phthalate ions and two water molecules.

### Introduction

The *o*-phthalate (pht) anion can act as a bridge when coordinating to metal atoms through both its carboxylate groups, giving rise to polymeric chains, whose

structures are affected by the presence of other ionic or molecular species.

The aim of the present research is to find what influence the alkaline cations, differing in radius and coordination, exert on the polymeric chains formed by pht anions coordinated to  $\text{Cu}^{II}$ .

Table 1. *Crystal data*

	$\text{Li}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ , diffractometer data, triclinic	$\text{Rb}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , diffractometer data, monoclinic	$\text{Cs}_2\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , photographic data, monoclinic
F.W.	477.74	598.78	693.64
Space group	$P\bar{1}$	$C2/c$	$C2/c$
$a$ (Å)	7.823 (7)	21.919 (15)	21.634 (18)
$b$ (Å)	10.935 (15)	7.827 (7)	8.068 (8)
$c$ (Å)	6.514 (10)	11.191 (10)	11.502 (13)
$\alpha$ (°)	111.8 (1)		
$\beta$ (°)	112.8 (1)	101.8 (3)	97.5 (3)
$\gamma$ (°)	87.4 (1)		
$V$ (Å <sup>3</sup> )	474.2	1879.2	1990.3
$Z$	1	4	4
$D_x, D_m$ (g cm <sup>-3</sup> )	1.67, 1.67	2.12, 2.12	2.31, 2.27
$F(000)$	243	1164	
$\mu$ (Mo $K\alpha$ ) (cm <sup>-1</sup> )	12.66	67.11	