References

Blake, C. C. F. (1967). *Proc. Roy. Soc.* B**167**, 435.

Blow, D. M. & Crick, F. H. C. (1959). *Acta Cryst.* **12**, 794.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Dickerson, R. E., Kendrew, J. C. & Strandberg, B. E. (1961). *Acta Cryst.* **14**, 1188.

Hoard, J. L. (1967). *Structural Chemistry and Molecular Biology*, p. 573. Edited by A. Rich & N. Davidson. San Francisco: Freeman.

Johnson, L. N. (1967). *Proc. Roy. Soc.* B**167**, 439.

Johnson, L. N. & Phillips, D. C. (1965). *Nature, Lond.* **206**, 761.

Lipscomb, W. N., Hartsuck, J. A., Reeke, G. N., Quiocho, F. A., Bethge, P. H., Ludwig, M. L., Steitz, T. A., Muirhead, H. & Coppola, J. C. (1968). *Brookhaven Symp. Biol.* **21**, 24.

Luzzati, V. (1953). *Acta Cryst.* **6**, 142.

Moffat, J. K. (1971). *J. Mol. Biol.* In the press.

Nobbs, C. L. (1966). *Hemes and Hemoproteins*, p. 143. Edited by B. Chance, R. W. Estabrook & T. Yonetani. London: Academic Press.

Nobbs, C. L., Watson, H. C. & Kendrew, J. C. (1966). *Nature, Lond.* **209**, 339.

Perutz, M. F. & Mathews, F. S. (1966). *J. Mol. Biol.* **21**, 199.

Perutz, M. F., Muirhead, H., Cox, J. M., Goaman, L. C. G., Mathews, F. S., McGandy, E. L. & Webb, L. E. (1968). *Nature, Lond.* **219**, 29.

Sigler, P. B., Jeffery, B. A., Matthews, B. W. & Blow, D. M. (1966). *J. Mol. Biol.* **15**, 175.

Sim, G. A. (1959). *Acta Cryst.* **12**, 813.

Sim, G. A. (1960). *Acta Cryst.* **13**, 511.

Steitz, T. A., Henderson, R. & Blow, D. M. (1969). *J. Mol. Biol.* **46**, 337.

Steitz, T. A., Ludwig, M. L., Quiocho, F. A. & Lipscomb, W. N. (1967). *J. Biol. Chem.* **242**, 4662.

Stryer, L., Kendrew, J. C. & Watson, H. C. (1964). *J. Mol. Biol.* **8**, 96.

Woolfson, M. M. (1956). *Acta Cryst.* **9**, 804.

Wyckoff, H. W., Hardman, K. D., Allewell, N. M., Inagami, T., Johnson, L. N. & Richards, F. M. (1967). *J. Biol. Chem.* **242**, 3984.

Acta Cryst. (1971). B**27**, 1420

The Crystal Structure of DL-Ornithine Hydrobromide*

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The crystal structure of DL-ornithine hydrobromide $NH_3(CH_2)_3.CH(NH_3^+).COO^-HBr$ has been determined using three-dimensional visual intensity data obtained with Cu $K\alpha$ radiation. The crystal belongs to the monoclinic system with cell dimensions $a=9{\cdot}388$; $b=7{\cdot}901$; $c=11{\cdot}663$ Å and $\beta=109°50'$. The space group is $P2_1/c$. The structure has been refined using the full-matrix least-squares method. Final R value is 7·3 % for the observed data. All the hydrogen atoms have been located from a difference Fourier synthesis. The standard deviation for the positions of the non-hydrogen atoms is about 0·008 Å. All bond lengths and angles are found to be normal. Both nitrogen atoms are protonated and the carboxyl group exists in the ionic form. The conformation and other aspects of the molecule are discussed.

Introduction

The determination of the crystal structure of amino acids, peptides and related compounds forms part of a major programme of research on the molecular structure of compounds of biological interest in this centre. Although ornithine is not one of the commonly occurring amino acids it is found in certain antibiotics. No detailed investigation of the structure of this compound appears to have been made earlier except in a complex form in ferrichrome (Zalkin, Forrester & Templeton, 1966). Therefore, it was decided to determine its structure. However, when the present investigation was nearing completion the analysis of the structure of L-ornithine hydrochloride by another group of workers (Chiba, Ueki, Ashida, Sasada & Kakudo, 1967) was brought to our notice. The final results of both these investigations are in good agreement. A note reporting the preliminary results of our present investigation has been published earlier (Kalyanaraman, 1967) and the full details are presented here.

Experimental

Crystals of DL-ornithine hydrobromide were obtained by dissolving DL-ornithine hydrobromide in a water-ethanol mixture and evaporating it under controlled humidity. Good crystals were obtained after several attempts; they were in the form of needles with *a* as the needle axis.

The unit-cell dimensions, space group and other data of this compound were obtained by the use of Weissenberg and Buerger precession techniques. The syste-

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matic absences were found to be *hkl*, no absences; *h*0*l*, absent for $l=2n+1$; 0*k*0, absent for $k=2n+1$. Thus the space group was fixed to be $P2_1/c$. The unit-cell parameters and other crystal data were as follows: $a=9\cdot388\pm0\cdot0094$; $b=7\cdot901\pm0\cdot008$, $c=11\cdot663\pm0\cdot013$ Å; $\beta=109°50'\pm15'$; $V=813\cdot6$ Å^{-3}; radiation used was Cu *Kα* ($\lambda=1\cdot5418$ Å).

The density as determined by flotation was 1·747 g.cm^{-3} leading to a formula weight of 213·9 with four molecules per unit cell. This agrees well with the calculated formula weight of 213·1.

The crystal used for collecting intensities was approximately a rectangular prism of dimensions $0\cdot1\times0\cdot015\times0\cdot021$ cm. Assuming a mean diameter of 0·018 cm the value of μR is 0·735. Therefore no absorption corrections were made. The crystal was mounted about the *a* axis and three-dimensional intensity data were collected for the eight layers 0*kl* to 7*kl* using the multiple-film and equi-inclination Weissenberg tecnhique with Cu *Kα* radiation. The intensities of 1320 reflexions were estimated visually by comparison with a calibrated strip.

The intensities were estimated on the elongated side of the film and were corrected for the Lorentz, polarization and spot size (Phillips, 1962). The scale and temperature factors were initially obtained using Wilson's (1942) method for each layer and were later refined by the least-squares method.

(We would like to thank the referee for bringing to our attention the fact that such a procedure is strictly incorrect (Lingafelter & Donohue, 1966). Therefore, little significance may be attached to the thermal parameters in Table 4; otherwise, the final results seem to be quite acceptable.)

Two of the reflexions, $40\bar{2}$ and $50\bar{2}$, were abnormally elongated due to the fact that a non-unique axis is the rotation axis. For these two only the integrated intensity was obtained by first matching the density with standard spots and applying the correction factor which was taken to be the ratio of the length of the streaks to the mean length of the other spots. The expected accuracy of these two reflexions was consequently less than for the others and was in fact noticed at the end of the analysis.

Refinement of the structure

The structure was solved by the heavy-atom method, the coordinates of the bromine having been determined from the Patterson projections along the three axes (Kalyanaraman, 1967). The reliability index for the initial model was found to be 27%, indicating that the structure was essentially correct.

Three cycles of initial refinement were carried out with isotropic temperature factors for all the atoms. The unobserved reflexions were included in the refinement, with $|F_o|=0$. The reliability index decreased to 16·8%. The unobserved reflexions were then given $|F_o|$ values as per Hamilton's (1955) scheme for a centrosymmetric case and a single cycle of refinement was accomplished. The *R* value was 13·5%. At this stage an examination of the reliability-index value for the different layers revealed that while the *R* value varied from about 8·5 to 16·5% for the layers zero to six respectively, the *R* value for the seventh layer alone had a high value of 35·6%. A close study of the collection of data showed that data for the seventh layer had been taken a few months after the data for the layers zero to six which were done in a single sequence. Fortunately, the crystal used was available for checking. The zero-layer photograph showed that the spots did not agree in intensity with the original zero-layer photographs. Presumably, the crystal had partly decomposed. The fairly close values of *R* for the remaining layers and the fact that the seventh layer alone had a high figure led us to the decision to exclude the seventh layer data from further refinements. Removal of the seventh layer data reduced the *R* value from 13·5 to 11·8%. One cycle of refinement was then carried out. The *R* value decreased to 10·3%.

Table 1. *Fractional coordinates and thermal parameters*† *of nonhydrogen atoms*

Values in parentheses are the standard deviations multiplied by 10^4.

The temperature factors for bromine is in the form

$$T=\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\right]$$

	x	*y*	*z*	*B*
O(1)	0·9184 (9)	1·1315 (8)	0·2657 (6)	3·164 Å^2
O(2)	1·0562 (10)	1·1306 (9)	0·1465 (6)	3·293
C(1)	1·0378 (12)	1·1561 (10)	0·2447 (7)	2·131
C(2)	1·1761 (11)	1·2147 (10)	0·3522 (7)	1·978
C(3)	1·2735 (12)	1·0620 (11)	0·4101 (8)	2·571
C(4)	1·1940 (12)	0·9521 (12)	0·4765 (8)	2·609
C(5)	1·2847 (11)	0·7944 (11)	0·5304 (7)	2·488
N(1)	1·2655 (10)	1·3367 (10)	0·3105 (7)	2·909
N(2)	1·1942 (10)	1·6756 (10)	0·5740 (7)	2·719
Br	1·4548 (1)	1·1281 (1)	0·1443 (1)	*

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
*	0·011968	0·010869	0·006531	0·000414	0·008562	0·000042

† In view of the method of scaling little significance can be attached to the anisotropic thermal parameters.

A difference Fourier synthesis was performed at this stage and it showed that the bromine had considerable anisotropy. It also gave all the 13 hydrogen atoms (Fig. 1). The peak height of the hydrogen atoms was above 0·5 e.Å^{-3}. Then, two cycles of refinement were carried out with the anisotropic temperature factor for bromine. Also, its scattering factor was changed to that of Br$^-$, and correction for its real part due to anomalous scattering ($\Delta f' = 0{\cdot}9$) was included. All the other atoms were given isotropic temperature factors only. The R value decreased to 8·9 %. Inclusion of hydrogen atoms in a structure-factor calculation with an average temperature factor of 2·75 Å^2 reduced the R value to 8·4 %. If unobserved reflexions were excluded the R value was 7·4 %. Up to this point, only a unit-weighting scheme had been adopted in refinement. Consequently, it was thought worthwhile to carry out a few cycles of least-squares refinement using an appropriate weighting scheme. Three cycles of least-squares refinement incorporating Cruickshank's weighting scheme were performed. The quantity minimized was $w(|F_o| - |F_c|)^2$. The weights were made equal to $1/\sigma^2$, where

$$\sigma = (A + |F_o| + C|F_o|^2 + D|F_o|^3)^{1/2} ,$$

with

$$A = 2\ |F_o|(\text{min});\ C = 0 \text{ and } D = 0.$$

The unobserved reflexions were completely excluded from the refinement and the hydrogen positions were not refined. The thermal parameters of the heavy-atom bromine only were refined anisotropically. The final R value at the end of the refinement was found to be 7·3%. Out of the 201 unobserved reflexions 35 have an F_c greater than the threshold value and the maximum ΔF was observed to be 5·5.

The final coordinates, thermal parameters and standard deviations are given in Table 1. The final shifts are very much less than the standard deviations, showing that the refinement had converged to the limits of accuracy. The coordinates of the hydrogen atoms are given in Table 2. The F_o data are presented in Table 3. The final electron-density map is shown in Fig. 2.

Table 2. *Coordinates of the hydrogen atoms in fractional units*

	x	y	z
H(1)	1·208	1·442	0·306
H(2)	1·356	1·361	0·367
H(3)	1·264	1·306	0·233
H(4)	1·167	0·717	0·642
H(5)	1·098	0·647	0·505
H(6)	1·247	0·563	0·593
H(21)	1·150	1·267	0·417
H(31)	1 368	1 103	0 469
H(32)	1 300	0 989	0·344
H(41)	1·208	1·008	0·556
H(42)	1·094	0·917	0·420
H(51)	1·400	0·833	0·583
H(52)	1·304	0·738	0·467

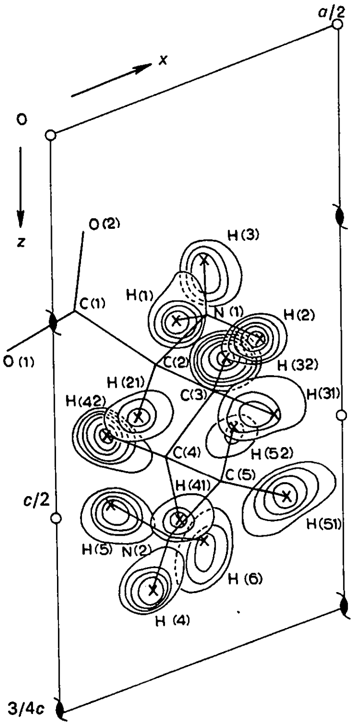

Fig. 1. Composite diagram of the difference Fourier synthesis viewed along the b axis. Contours are at intervals of 0·1e.Å^{-3} with initial contour at 0·3e.Å^{-3}.

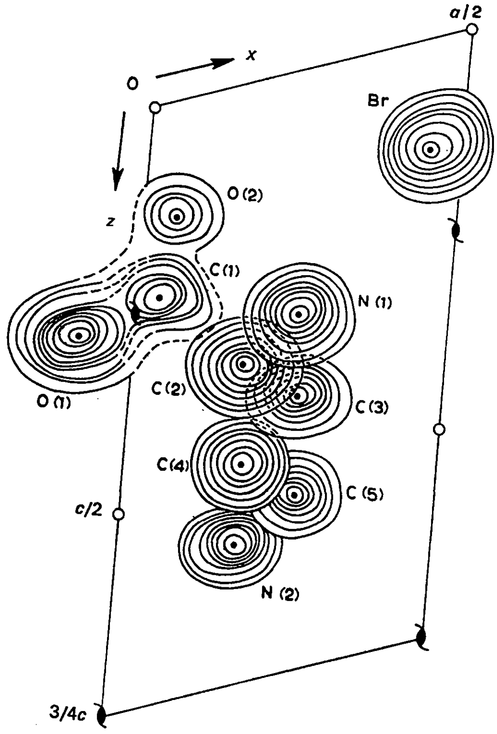

Fig. 2. Composite diagram of the final three-dimensional electron-density function viewed along the b axis. Contours are drawn at intervals of 1e.Å^{-3}. In the position of the bromine atom the contour intervals are arbitrary.

The program used was *PROGRAM LALS* originally written by Gantzel, Sparks & Trueblood (1961) and modified by Zalkin, Lundgren, Liminga & Brändén for the CDC-3600 computer. The scattering factors used for Br^-, O, N, C and H were those listed in *International Tables for X-ray Crystallography* (1962).

Discussion of the structure

Bond lengths and angles

The bond lengths and angles in the molecule are shown in Fig. 3. The average estimated standard deviations for the C–O, C–N and C–C bonds are 0·013, 0·013, and 0·014 Å respectively. The mean standard

Table 3. *Observed and calculated structure factors*

h	k	l	F_o	F_c
0	0	2	43.3	-37.5
0	0	4	84.6	-77.6
0	0	6	46.1	42.5
0	0	8	43.0	38.7
0	0	10	47.5	-47.5
0	1	1	34.1	32.3
0	1	2	32.6	-31.4
0	1	3	97.7	-104.5
0	1	4	41.7	41.3
0	1	5	15.1	-12.2
0	1	6	59.7	58.2
0	1	7	48.1	48.2
0	1	8	38.8	-37.7
0	1	9	18.4	-17.5
0	1	10	14.0	-12.6
0	1	11	19.1	-18.1
0	1	12	21.4	18.3
0	1	13	11.2	9.5
0	2	0	45.2	-43.3
0	2	1	136.5	-131.8
0	2	2	18.3	17.1
0	2	3	19.4	-19.8
0	2	4	4.9	4.3
0	2	5	73.9	74.0
0	2	7	16.4	15.7
0	2	9	56.5	-62.3
0	2	10	9.7	9.7
0	2	11	22.0	23.3
0	2	13	13.1	11.1
0	3	1	80.9	-76.1
0	3	2	74.3	-75.8
0	3	3	72.9	72.8
0	3	4	26.7	25.4
0	3	5	15.5	14.6
0	3	6	33.2	34.6
0	3	7	35.1	-37.3
0	3	8	43.6	-46.3
0	3	9	12.3	13.7
0	3	10	13.7	-12.8
0	3	11	12.2	10.4
0	3	12	16.1	16.0
0	3	13	11.2	-10.0
0	4	0	124.3	-115.5
0	4	1	3.9	6.0
0	4	2	54.9	51.0
0	4	3	9.8	-7.9
0	4	4	51.9	54.2
0	4	6	26.6	-26.6
0	4	7	6.6	4.7
0	4	8	25.1	-27.4
0	4	9	23.4	25.0
0	4	10	27.1	31.1
0	5	1	35.4	-31.7
0	5	2	54.4	52.5
0	5	3	41.7	38.1
0	5	4	22.0	-21.3
0	5	6	40.7	-43.4
0	5	7	38.5	-42.0
0	5	8	21.5	24.9
0	5	9	9.2	9.3
0	5	10	6.8	6.5
0	5	11	16.4	16.6
0	5	12	14.2	-16.9
0	6	0	22.4	22.3
0	6	1	55.5	53.4
0	6	2	12.8	-11.9
0	6	3	10.2	10.5
0	6	5	33.9	-36.5
0	6	9	26.5	28.4
0	6	11	9.3	-11.2
0	7	1	34.9	37.6
0	7	2	33.6	34.2
0	7	3	32.0	-34.5
0	7	4	11.2	-9.7
0	7	6	13.8	-14.9
0	7	7	26.1	27.4
0	7	8	8.9	11.0
0	7	9	7.2	-7.6
0	8	0	26.2	29.2
0	8	2	17.4	-18.2
0	8	4	26.2	-25.3
0	8	6	17.8	17.9
0	8	7	9.1	8.8
0	8	8	13.3	14.8
0	9	1	7.8	7.6
0	9	2	27.8	-25.8
0	9	3	7.2	-8.4
0	9	5	4.9	-4.8
0	9	6	10.3	12.2
0	10	0	8.5	-8.8
0	10	1	16.1	-20.5
1	0	0	25.4	-33.7
1	0	2	28.5	-25.1
1	0	4	71.9	75.8
1	0	6	40.3	-41.7
1	0	8	21.3	-20.6
1	0	10	11.8	12.4
1	0	12	20.3	19.4
1	1	0	29.4	-26.5
1	1	1	67.8	-62.8
1	1	2	110.8	119.6
1	1	3	5.3	4.3
1	1	4	15.4	14.6
1	1	5	14.6	13.5
1	1	6	51.0	-53.0
1	1	7	32.2	-30.2
1	1	8	16.7	15.6
1	1	10	12.5	12.7
1	1	11	20.3	19.5
1	1	12	17.7	-17.1
1	1	13	7.8	-7.4
1	2	0	10.0	-9.9
1	2	1	11.2	10.9
1	2	2	23.8	21.5
1	2	3	99.2	101.5
1	2	4	35.8	30.2
1	2	5	88.6	-91.6
1	2	6	17.4	16.0
1	2	7	5.7	-5.5
1	2	9	20.7	23.8
1	2	13	10.0	-10.4
1	3	0	23.9	-33.3
1	3	1	27.7	29.1
1	3	2	30.2	31.5
1	3	3	35.1	-33.9
1	3	5	24.7	-25.4
1	3	6	21.5	-21.9
1	3	7	23.3	22.9
1	3	8	15.9	16.9
1	3	10	9.5	8.7
1	3	11	26.4	-25.8
1	3	12	12.6	-11.6
1	4	0	44.8	47.3
1	4	1	8.9	6.3
1	4	2	29.6	30.8
1	4	3	18.2	-15.0
1	4	4	69.5	-68.7
1	4	5	11.9	7.6
1	4	6	26.1	23.8
1	4	7	6.2	-7.8
1	4	8	21.6	22.3
1	4	9	4.3	5.4
1	4	10	13.7	-12.8
1	4	12	13.9	-13.9
1	5	0	15.2	15.8
1	5	1	25.8	29.8
1	5	2	42.7	-43.7
1	5	3	21.6	-21.3
1	5	4	11.8	9.8
1	5	5	10.6	-9.0
1	5	6	35.2	37.3
1	5	7	21.6	21.6
1	5	8	11.5	-11.1
1	5	10	9.4	-10.1
1	6	1	16.2	-17.1
1	6	2	11.9	-11.4
1	6	3	47.9	-51.0
1	6	5	31.4	33.2
1	6	6	9.9	-6.1
1	6	9	19.3	-18.8
1	6	10	2.2	-0.6
1	7	0	11.0	11.0
1	7	1	15.3	-16.6
1	7	2	12.6	-12.5
1	7	3	20.6	20.2
1	7	6	12.3	13.4
1	7	7	18.5	-16.6
1	7	8	6.5	-7.2
1	8	0	24.8	-26.6
1	8	2	11.2	-9.1
1	8	3	16.2	14.9
1	8	4	31.0	30.0
1	8	5	12.0	-10.8
1	8	6	11.2	-9.3
1	8	8	8.2	-10.3
1	9	1	14.3	-13.1
1	9	2	17.5	15.9
1	9	3	18.7	16.4
1	9	5	15.3	14.2
1	9	6	7.8	-11.4
1	1	-1	17.5	-16.8
1	1	-2	19.8	-16.9
1	1	-3	107.2	110.5
1	1	-4	72.3	77.3
1	1	-5	16.7	-12.9
1	1	-6	7.9	6.3
1	1	-7	44.2	-40.8
1	1	-8	32.8	-32.3
1	1	-9	17.0	16.2
1	1	-11	12.3	14.8
1	1	-12	24.7	21.1
1	1	-13	8.4	-10.1
1	2	-1	48.6	-52.1
1	2	-3	37.1	-36.8
1	2	-4	30.2	-27.6
1	2	-5	45.7	46.2
1	2	-7	42.7	-40.5
1	2	-9	27.9	-26.5
1	2	-11	16.1	20.2
1	2	-12	9.7	-7.3
1	2	-13	17.2	15.9
1	3	-1	21.3	20.4
1	3	-2	44.7	-46.1
1	3	-3	82.3	-81.8
1	3	-4	48.7	45.7
1	3	-5	20.6	19.3
1	3	-6	22.7	20.6
1	3	-7	46.5	44.9
1	3	-8	19.8	-18.8
1	3	-9	14.4	-14.7
1	3	-12	12.7	14.6
1	3	-13	18.6	17.3
1	4	-1	10.0	-9.2
1	4	-2	27.9	-27.8
1	4	-3	6.7	4.4
1	4	-4	61.5	-58.9
1	4	-6	66.3	61.8
1	4	-10	25.5	-27.6
1	4	-12	9.3	6.6
1	4	-13	7.0	-7.1
1	5	-1	20.2	17.2
1	5	-2	39.4	35.2
1	5	-3	38.0	-39.1
1	5	-4	18.9	-16.9
1	5	-6	8.7	3.2
1	5	-7	14.1	13.5
1	5	-8	27.5	23.6
1	5	-9	9.9	-9.6
1	5	-11	19.3	-15.3
1	5	-12	18.8	-16.3
1	6	-1	36.4	37.0
1	6	-4	27.5	21.9
1	6	-5	62.2	-58.2
1	6	-6	14.3	-11.3
1	6	-7	15.0	13.4
1	6	-9	20.6	17.1
1	6	-11	13.5	-13.5
1	7	-1	19.5	-17.4
1	7	-2	33.7	31.9
1	7	-3	27.2	27.5
1	7	-4	19.2	-17.0
1	7	-6	10.5	-7.1
1	7	-7	17.0	-14.6
1	7	-8	16.4	14.5
1	7	-9	12.7	12.3
1	8	-2	16.2	15.2
1	8	-4	22.8	19.0
1	8	-6	27.9	-23.6
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5	3	-8	27.9	-25.2
5	3	-9	42.5	-43.0
5	3	-10	29.6	25.6
5	3	-11	19.5	16.9
5	4	-1	11.5	10.6
5	4	-2	59.7	-66.2
5	4	-3	6.3	-5.9
5	4	-4	23.5	22.9
5	4	-5	6.9	6.4
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5	5	-2	6.9	-7.1
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5	5	-4	22.6	-21.7
5	5	-5	34.8	32.8
5	5	-6	24.6	23.7
5	5	-7	7.2	-4.7
5	5	-8	24.1	21.4
5	5	-9	26.2	-24.0
5	5	-10	29.6	-25.9
5	5	-11	9.6	7.6
5	6	-1	33.8	32.5
5	6	-2	7.2	7.5
5	6	-3	43.1	-44.6
5	6	-5	21.0	-19.7
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5	6	-7	26.0	24.4
5	6	-10	8.6	3.6
5	6	-11	28.7	-24.3
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5	7	-3	12.9	11.0
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5	7	-5	27.4	-24.1
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5	7	-8	18.6	15.0
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5	7	-10	9.0	-8.4
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5	9	-1	5.9	4.7
5	9	-2	4.9	2.7
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5	3	6	17.9	-16.9
5	3	8	7.2	-5.4
5	3	9	15.9	13.8
5	3	10	8.3	9.0
5	4	0	17.2	16.4
5	4	1	17.2	17.8
5	4	2	33.2	34.6
5	4	3	10.1	-10.5
5	4	4	21.5	-21.3
5	4	5	21.5	-15.9
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5	5	0	38.6	41.9
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5	5	2	20.7	-21.1
5	5	3	18.6	18.4
5	5	4	28.8	-29.0
5	5	5	25.0	-20.8
5	5	6	20.3	15.7
5	5	7	6.9	3.7
5	5	8	7.2	4.7
5	6	1	16.0	15.0
5	6	3	24.9	-22.6
5	6	4	6.3	-1.9
5	6	5	5.9	5.0
5	6	6	5.3	-3.2
5	6	7	17.9	16.8
5	7	0	13.4	12.1
5	7	1	26.9	-22.4
5	7	3	9.3	-6.9
5	7	4	14.4	-11.7
5	7	5	19.5	16.5
5	7	6	7.6	8.0
5	8	0	9.6	-6.8
5	8	2	22.9	-20.6
5	8	3	5.3	7.3
5	8	4	8.0	8.3
5	9	0	14.5	-16.9
5	9	1	5.3	-6.9
5	0	0	19.7	-13.2
5	0	2	48.9	-49.3
5	0	4	25.2	24.8
5	0	6	23.6	29.8
5	0	8	26.7	-27.2
5	0	10	10.7	-12.6
6	0	-2	21.5	-21.2
6	0	-4	22.7	24.3
6	0	-6	37.7	36.7
6	0	-8	51.5	-58.3
6	0	-12	27.7	-25.3
6	1	-1	24.9	-26.3
6	1	-2	17.5	-17.8
6	1	-3	10.6	-9.8
6	1	-4	36.3	-43.1
6	1	-5	35.7	36.5
6	1	-6	39.2	37.7
6	1	-7	13.0	-12.1
6	1	-8	7.8	-6.2
6	1	-9	13.3	-12.8
6	1	-10	14.5	-13.3
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6	2	-11	18.5	-19.0
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6	2	-13	19.2	14.6
6	3	-1	16.2	12.9
6	3	-2	4.0	3.9
6	3	-3	4.9	-4.9
6	3	-4	25.2	-23.3
6	3	-5	39.0	-40.1
6	3	-6	27.5	26.5
6	3	-7	18.3	15.4
6	3	-8	10.2	9.0
6	3	-9	21.7	19.6
6	3	-10	18.3	-19.0
6	3	-12	4.1	-1.5
6	3	-13	13.0	-13.4
6	4	-1	22.9	-23.7
6	4	-2	25.1	22.3
6	4	-4	25.5	-23.5
6	4	-5	4.7	5.0
6	4	-6	27.1	-26.3
6	4	-8	33.2	33.2
6	4	-12	20.7	-20.9
6	5	-1	24.8	24.5
6	5	-2	12.9	11.3
6	5	-3	16.5	16.3
6	5	-4	34.7	37.2
6	5	-5	19.9	-20.0
6	5	-6	26.0	-26.5
6	5	-7	6.0	6.2
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6	5	-10	17.0	15.7
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6	6	-1	8.4	-6.5
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6	7	-10	8.5	13.3
6	8	-2	17.6	-17.2
6	8	-3	7.6	-7.2
6	8	-4	8.4	8.3
6	8	-5	12.0	13.4
6	1	0	33.5	31.3
6	1	1	18.4	14.2
6	1	2	5.3	4.9
6	1	3	19.3	17.3
6	1	4	26.2	-24.2
6	1	5	25.9	-25.6
6	1	6	4.9	-1.0
6	1	7	11.9	-10.0
6	1	8	8.4	5.6
6	1	9	6.3	6.1
6	2	0	4.8	-3.9
6	2	1	35.8	39.5
6	2	3	27.8	-26.2
6	2	4	6.9	7.0
6	2	5	4.9	-1.3
6	2	6	4.8	5.2
6	2	7	14.9	12.7
6	3	0	33.4	36.9
6	3	1	7.8	-6.0
6	3	3	20.9	-19.8
6	3	4	18.5	-16.4
6	3	5	21.6	21.5
6	3	6	9.6	8.3
6	3	7	4.9	3.8
6	3	8	8.1	7.5
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6	4	0	21.7	20.2
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6	4	6	21.0	19.1
6	4	7	4.4	1.4
6	4	8	4.5	-5.7
6	5	0	21.3	-20.1
6	5	1	20.1	-18.7
6	5	3	8.5	-8.2
6	5	4	14.2	12.1
6	5	5	8.8	6.6
6	5	6	9.5	-7.5
6	6	0	4.8	-1.7
6	6	1	22.6	-22.7
6	6	2	5.6	3.0
6	6	3	22.2	19.3
6	6	5	9.1	8.8
6	6	6	5.5	-6.9
6	7	0	11.1	-9.3
6	7	1	10.0	7.6
6	7	3	9.2	8.4
6	7	4	9.3	8.3
6	8	0	5.7	-5.7
6	8	2	13.3	17.5
6	0	0	23.5	-20.0
6	0	2	46.1	44.4
6	0	4	14.5	-13.9
6	0	6	15.9	-14.2
6	0	9	28.2	21.7

deviation of angles involving light atoms is 0·8°. The bond lengths observed were found to be quite normal. The average C–C length in the structure is 1·528 Å which agrees well with the average (1·530 Å) in L-ornithine hydrochloride (Chiba, Ueki, Ashida, Sasada & Kakudo, 1967). The observed C(1)–C(2) distance of 1·539 Å which is also close to 1·540 Å in L-ornithine HCl (Chiba *et al.*) appears to be slightly greater than the weighted average of 1·527 Å as given by Marsh & Donohue (1967) although Ramachandran & Lakshminarayanan (1966) give a value of 1·540 Å. The mean C–C distance in the aliphatic side chain is 1·521 Å and it agrees with the weighted average of 1·530 Å in the side chain of arginine (Marsh & Donohue, 1967).

The difference Fourier synthesis (Fig. 1) clearly indicates that both the nitrogen atoms are protonated. The mean of the two C–N distances, namely 1·467 Å, agrees with the weighted average of 1·487 Å given by Marsh & Donohue (1967).

The mean value of the tetrahedral angles is 110·6°. It is pertinent to remark that while in a number of amino acid structures the value of the angle C(2)–C(3)–C(4) is slightly larger than the tetrahedral value of 114° (Ramachandran & Lakshminarayanan, 1966), the present observed value is 110·7°. All other angles are normal within the limits of accuracy.

The hydrogen positions were obtained by the final difference Fourier synthesis. No refinement of these positions was made; hence, a discussion of the C–H and N–H distances is not worth while.

Least-squares plane

The molecule is broadly characterized by two planar groups. The first one involves the carboxyl group [atoms O(1), O(2), C(1) and C(2)] and the other one involves the side-chain atoms C(2), C(3), C(4), C(5), N(2) and N(1). The least-squares plane of the carboxyl group is given by the equation

$$-0{\cdot}1859\,X'+0{\cdot}9504\,Y'-0{\cdot}2497\,Z'=0{\cdot}6021. \quad (1)$$

The deviations of the atoms from plane (1) are O(1), −0·005 Å; O(2), −0·006 Å; C(1), 0·014 Å and C(2), −0·003 Å. The least-squares plane involving the second group of atoms is

$$0{\cdot}0280\,X'+0{\cdot}4905\,Y'+0{\cdot}8710\,Z'=8{\cdot}1369\,. \quad (2)$$

The deviations in Å of the atoms from plane (2) are N(1), 0·046; N(2), −0·046; C(2), −0·056; C(3), −0·076; C(4), 0·104; and C(5), 0·026. In equations (1) and (2) X', Y', and Z' correspond to the rectangular coordinate system and the corresponding transformations are $X'=X+Z\cos\beta$, $Y'=Y$, $Z'=Z\sin\beta$.

The planarity of the second group arises basically out of the fully extended (*trans*) configuration of the side chain. The atom N(1) is only about 0·046 Å away from plane (2) while the deviation from plane (1) is 0·842 Å. The corresponding deviation of N(1) from plane (1) in L-ornithine hydrochloride (Chiba *et al.*, 1967) is 0·838 Å. The dihedral angle between planes (1) and (2) is 75°55′, and the corresponding angle in L-ornithine hydrochloride is 78°42′. These values are close to those found in a similar structure where the aliphatic side chain has a fully extended configuration. Thus, the angle is 71°24′ in lysine hydrochloride dihydrate (Wright & Marsh, 1962) and 74° in arginine dihydrate (Karle & Karle, 1964).

Crystal packing and hydrogen bonding

Six independent hydrogen atoms belong to the two nitrogen atoms which take part in hydrogen bonding. The details are given in Table 4. The nitrogen N(1) bonds with two bromine atoms and one oxygen atom whereas N(2) bonds with one bromine atom and two oxygen atoms (Fig. 4).

Table 4. *Hydrogen bond distances and angles*

Symmetry code:

(i)	x	y	z	(iv)	$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(ii)	$\bar{x}$	$\bar{y}$	$\bar{z}$	(v)	$\bar{x}-1$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(iii)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(vi)	$x-1$	$\frac{1}{2}+y$	$\frac{1}{2}+z$

N(1)–Br(i)	3·46 Å	C(2)–N(1)–Br(i)	109·5°
N(1)–Br(iv)	3·40	C(2)–N(1)–Br(iv)	153·4
N(1)–O(1) (v)	2·86	C(2)–N(1)–O(1) (v)	106·6
N(2)–Br(iii)	3·33	C(5)–N(2)–Br(iii)	94·8
N(2)–O(1) (vi)	2·88	C(5)–N(2)–O(2) (v)	99·4
N(2)–O(2) (v)	2·86	C(5)–N(2)–O(1) (vi)	105·7

Thus, the overall stability of the structure appears to arise mainly from a three-dimensional network of six hydrogen bonds. The packing of the molecule down the *b* axis is given in Fig. 5. No unusual short contacts are in the structure.

Conformation of the ornithine molecule

The general molecular configuration of ornithine appears to be the same as that of arginine and lysine. Lysine $HCl.2H_2O$ (Wright & Marsh, 1962) and arginine (Karle & Karle, 1964) have a fully extended side-chain configuration. In describing the conformations

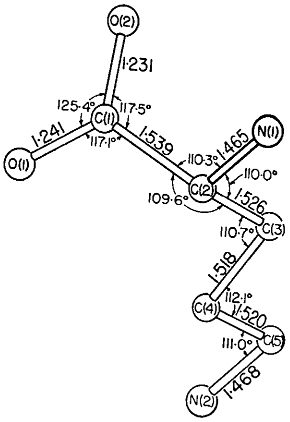

Fig. 3. Observed bond lengths and bond angles.

of the present molecule the notation of Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga (1966) is followed.

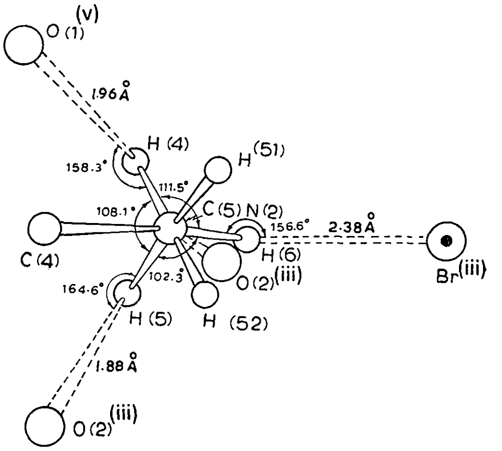

Fig. 4. Environment of N(2) as seen along C(5)–N(2) bond.

The angles $\psi 1$ and $\psi 2$ which are the torsion angles around the bond C–C′* are 143·1 and 320·1° Fig. 6(*a*). The corresponding values in L-ornithine hydrochloride (Chiba *et al.*, 1967) are found to be 144·1 and 321·5°. This clearly shows that the plane N(1)–C$^\alpha$–C′ is tilted relative to O(2)–C′–C$^\alpha$ by about 40·1°. Tilting of this order is not uncommon. For example in L-arginine hydrochloride (Ramachandran, Mazumdar, Venkatesan & Lakshminarayanan, 1966) the corresponding values are $\psi 1 = 134{\cdot}3°$ and $\psi 2 = 309{\cdot}1°$ for molecule I and $\psi 1 = 138{\cdot}3°$ and $\psi 2 = 319{\cdot}2°$ for molecule II.

According to Ramachandran & Lakshminarayanan (1966) the C$^\gamma$ atoms can occupy all the staggered positions I, II and III although positions I and III are less likely. However, in the several derivatives of arginine, Ramachandran *et al.* (1966) have found that the γ-carbon occupies all the three positions. In the present investigation the γ-carbon atom occupies position II

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* C′ = C(1); C$^\alpha$ = C(2); C$^\beta$ = C(3); C$^\gamma$ = C(4); C$^\delta$ = C(5) N = N(2).

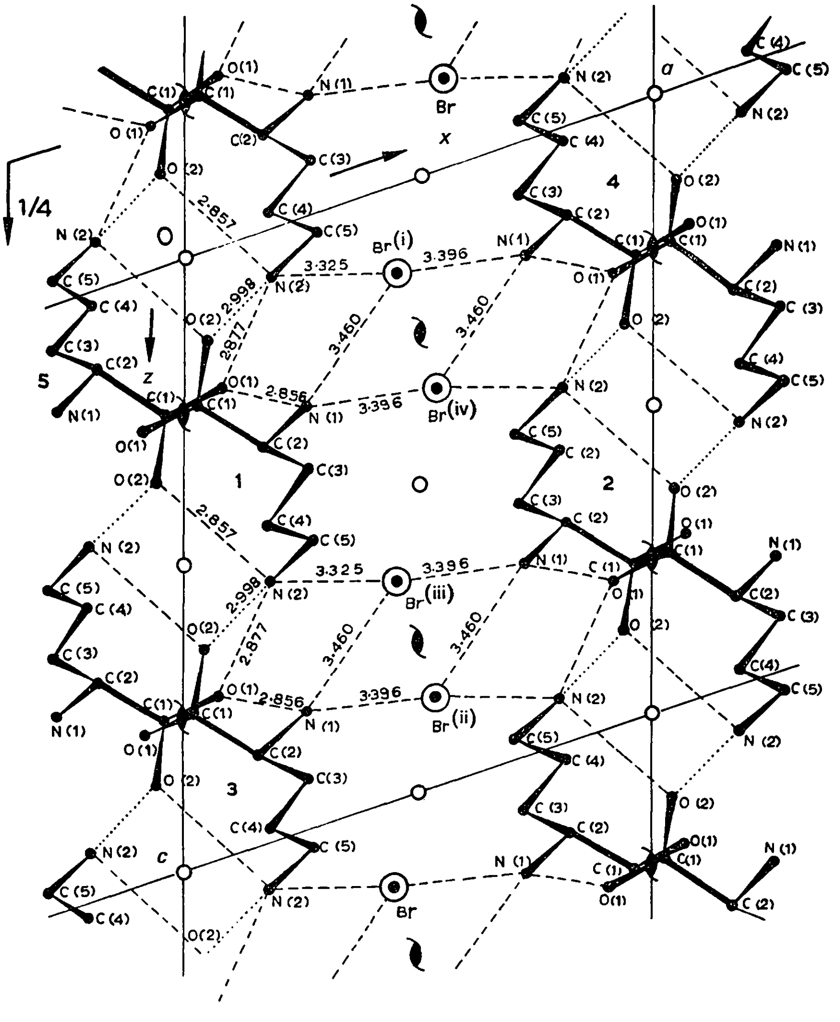

Fig. 5. View of the structure projected down the *b* axis.

(which is the most favoured position) as also in L-ornithine hydrochloride. The L-ornithine residues in ferrichrome (Zalkin *et al.*, 1966) have the following conformations. In residues 3 and 4 the γ-carbon atoms prefer position III. The relevant χ^i values of different ornithine structures so far solved are given in Table 5, which shows that as in the case of arginine derivatives the γ-carbon atom in ornithine residues appears in all the three positions. The side-chain conformations of the ornithine residue as it appears in five different cases are as follows:

Ornithine 2 ferrichrome	I	II	III
3	III	I	I
4	III	II	III
L-ornithine HCl	II	II	II
DL-ornithine HBr	II	II	II

Thus, while L-ornithine hydrochloride and DL-ornithine hydrobromide prefer a fully extended *trans* conformation for the side chain, the side chains of the ornithine residues in ferrichrome do not. This might be due to the presence of large substituents on the

Table 5. *Torsion angles observed in ornithines so far solved*

	ψ_1	ψ_2	χ^1	χ^2	χ^3
* Ornithine 2 (ferrichrome)A	—	27·2°	55·4°	177·1°	303·7°
Ornithine 3 (ferrichrome)A	131·6°	—	300·7	76·2	45·4
Ornithine 4 (ferrichrome)A	183·6	—	299·7	149·0	303·8
L-Ornithine hydrochloride	144·1	321·5	187·2	186·9	174·9
† DL-Ornithine hydrobromide	143·1	320·1	191·6	182·6	169·5

* Values taken from Lakshminarayanan, Sasisekharan & Ramachandran (1967).
† The coordinates of an L-molecule are chosen.

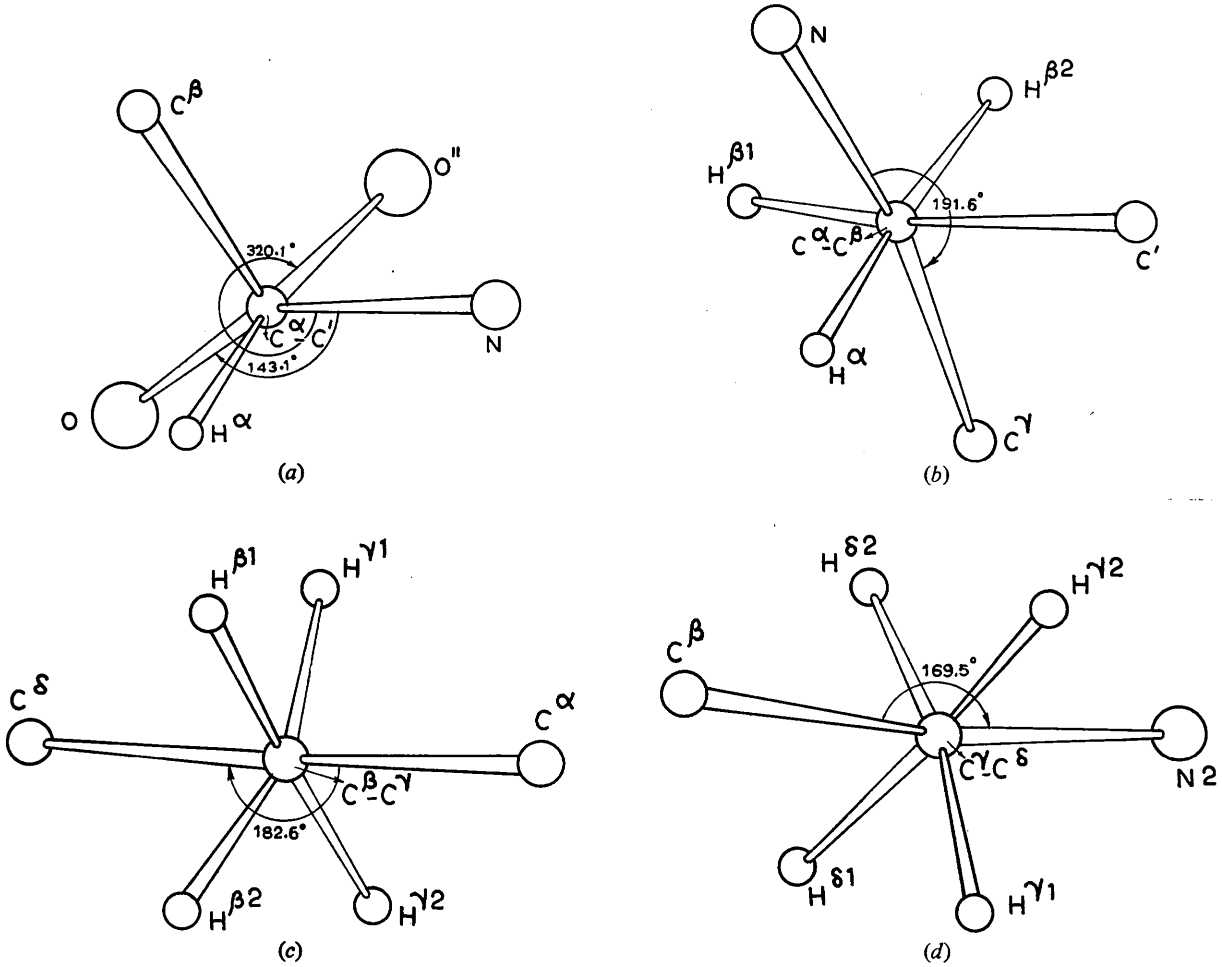

Fig. 6. View along (*a*) C^α–C′, (*b*) C^α–C^β, (*c*) C^β–C^γ and (*d*) C^γ–C^δ.

terminal nitrogen atom. In the present investigation the χ^i values correspond to position II and they are 191·6°, 182·6° and 169·5° (Fig. 6(*b*), (*c*) and (*d*) respectively) and their average is 181·2°. This agrees well with the average of 184° given by Ramachandran and Lakshminarayanan.

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References

CHIBA, A., UEKI, T., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1967). *Acta Cryst.* **22**, 863.

EDSALL, J. T., FLORY, P. J., KENDREW, J. C., LIQUORI, A. M. NÉMETHY, G., RAMACHANDRAN, G. N. & SCHERAGA, H. A. (1966). *J. Mol. Biol.* **15**, 399.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *PROGRAM LALS.*

HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

KALYANARAMAN, A. R. (1967). *Curr. Sci.* **36**, No. 7, 168.

KARLE, I. L. & KARLE, J. (1964). *Acta Cryst.* **17**, 835.

LAKSHMINARAYANAN, A. V., SASISEKHARAN, V. & RAMACHANDRAN, G. N. (1967). *In Conformation of Biopolymers*, Vol. 1, p. 61, Edited by G. N. RAMACHANDRAN. London: Academic Press.

LINGAFELTER, E. C. & DONOHUE, J. (1966). *Acta Cryst.* **20**, 321.

MARSH, R. E. & DONOHUE, J. (1967). *Advanc. Protein Chem.* **22**, 235.

PHILLIPS, D. C. (1962). *International Tables for X-ray Crystallography.* Vol. III, p. 140. Birmingham: Kynoch Press.

RAMACHANDRAN, G. N. & LAKSHMINARAYANAN, A. V. (1966). *Biopolymers*, **4**, 495.

RAMACHANDRAN, G. N., MAZUMDAR, S. K., VENKATESAN, K. & LAKSHMINARAYANAN, A. V. (1966). *J. Mol. Biol.* **15**, 232.

WILSON, A. J. C. (1942). *Nature, Lond.*, **150**, 152.

WRIGHT, W. B. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 54.

ZALKIN, A., FORRESTER, J. D. & TEMPLETON, D. H. (1966). *J. Amer. Chem. Soc.* **88**, 1810.

Acta Cryst. (1971). B**27**, 1427

The Crystal Structures of Nitrates of Divalent Hexaquocations. III. Hexaquonickel nitrate

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The crystals of hexaquonickel nitrate, $Ni(OH_2)_6(NO_3)_2$, are triclinic, space group $P\bar{1}$ with the following unit-cell constants: $a = 7{\cdot}694$, $b = 11{\cdot}916$, $c = 5{\cdot}817$ Å; $\alpha = 102{\cdot}3$, $\beta = 102{\cdot}4$, $\gamma = 105{\cdot}9°$, $Z = 2$. The structure consists of hexaquonickel cations and nitrato anions joined to one another by a network of hydrogen bonds. The symmetry of the cation is nearly octahedral deformed to an orthorhombic bipyramid, with pairs of opposite distances $Ni–OH_2 = 2{\cdot}03$, 2·07, 2·09 Å. The nitrato anions are not exactly trigonal; they present, in both crystallographically independent anions, two short bonds with average $N–O = 1{\cdot}23$ Å and one long bond $N–O = 1{\cdot}28$ Å. Not all the water molecules form equal hydrogen bonds, either in direction or in strength. The packing of the cation and anion units in the nickel compound cannot be reduced to the same scheme as the zinc and magnesium nitrates. On the whole there are significant differences compared with the structure of $Zn(OH_2)_6(NO_3)_2$ and $Mg(OH_2)_6(NO_3)_2$ in (i) environment of hexaquocation, (ii) structure of nitrato anions and (iii) packing.

Introduction

The crystals of nitrates of divalent hexaquocations $Zn(OH_2)_6(NO_3)_2$ (Ferrari, Braibanti, Manotti Lanfredi & Tiripicchio, 1967), $Mg(OH_2)_6(NO_3)_2$ (Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli, 1969), $Ni(OH_2)_6(NO_3)_2$ (Jayaraman, 1957; Weigel, Imelik & Laffitte, 1962; Weigel, Imelik & Prettre, 1964) and $Co(OH_2)_6(NO_3)_2$ (Weigel, Imelik & Prettre, 1964) are not isostructural. This is rather surprising because the structures of these cations are generally assumed to be octahedral and of similar size. It is not clear yet if the differences are due either to different types of bonding of water molecules with the metal ion or to packing strains or to other causes such as the thermal energy state of the nitrato groups.

Experimental

Preparation

Crystals of the compound were obtained in the form of needles or elongated plates by evaporation of an aqueous solution at room temperature. The crystals are very often twinned. They are hygroscopic and had to be sealed in Lindemann capillary tubes for the crystal analysis.