

Pauling for having suggested this problem and for his constructive criticism of the manuscript.

Summary

The unit cell, the probable space group, and the x and z atomic parameters for the monoclinic crystals of copper *dl*- α -aminobutyrate have been determined by X-ray diffraction methods. The Patterson projection $p(x,z)$ has the appearance of the Fourier projection $\rho(x,z)$, because of the

presence of the heavy copper atoms in the special centrosymmetric positions of the probable space group $C_{2h}^5-P_c^2$. Although the y parameters have not been determined the existence has been shown of coplanar coordination of carboxyl oxygen atoms and amino nitrogen atoms around the copper atoms, and the presence of oxygen-to-nitrogen hydrogen bonds in the x and z plane is evident.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 15, 1944

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 987]

The Crystal Structure of Nickel Glycine Dihydrate

BY A. J. STOSICK

Introduction.—As a part of the program of protein and amino acid research undertaken in these laboratories, the crystal structure of the dihydrated nickel salt of glycine has been determined by X-ray methods. The investigation, which was begun in the fall of 1939, was substantially completed by the spring of 1941, when the assumption of other duties by the author caused the work to be discontinued. It is the purpose of this paper to present the results of the investigation, since there is little likelihood that the investigation will be resumed in order to refine the parameters.

The purpose of investigating nickel glycine dihydrate was twofold: first, to make a comparison of the structure of the glycine residue in the salt with that for glycine itself as determined by Albrecht and Corey¹; and second, to determine whether the presence of the metal atom facilitates the structure determination. The use of a metal as an aid in determining the structure of complex organic substances has been discussed previously.^{2,3}

The crystals used in this investigation were prepared by placing an excess of nickel carbonate in a warm aqueous solution of glycine. The solution was then filtered and the solvent was allowed to evaporate slowly. The crystals have previously been reported by Bruni.⁴ Accurate optical goniometry was not possible with the crystals although superficially their faces were well defined. After a preliminary coarse optical orientation the final adjustment of the crystal orientation was made by means of preliminary X-ray photographs. The faces appearing on the crystals appear to be those for the planes $\{100\}$, $\{\bar{1}00\}$, $\{011\}$, $\{0\bar{1}\bar{1}\}$, $\{0\bar{1}1\}$, and $\{0\bar{1}\bar{1}\}$, but this identification has not been confirmed.

(1) G. Albrecht and R. B. Corey, *THIS JOURNAL*, **61**, 1087 (1939).

(2) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936);

J. M. Robertson and I. Woodward, *ibid.*, 219 (1937).

(3) A. J. Stosick, *THIS JOURNAL*, **67**, 362 (1945).

(4) Bruni, *Atti della Reale Accademia dei Lincei*, [5] **13**, II, 27; cf. Beilstein also.

The Unit Cell and Space Group.—A cursory optical examination showed that the crystals are anisotropic, and suggested that they exhibit monoclinic symmetry. Examination of Laue, rotation and equi-inclination Weissenberg photographs of the crystals led to the following monoclinic unit cell and probable space group

$$\begin{array}{ll} a = 7.60 \pm 0.02 \text{ \AA} & \beta' = 63^\circ 25' \\ b = 6.60 \pm .02 \text{ \AA} & Z = 2 \\ c = 9.63 \pm .02 \text{ \AA} & C_{2h}^5 - P_c^2 \end{array}$$

The length of the b axis was calculated from the spacings of layer lines on a b axis rotation photograph. The lengths of the a and c axes were determined from the spacings of equatorial reflections on the same photograph. The acute monoclinic angle β' was also determined from equatorial reflections on this same photograph; four different sets of reflections gave values differing by a maximum of only $0^\circ 8'$. The density of the crystals, measured by the flotation method, was found to be 1.86 g./cc. This density corresponds to 1.99 molecules of the formula $Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$ in each unit cell, and if the indicated space group is correct the metal atoms must be located at centers of symmetry.

The space group assigned to the crystals $C_{2h}^5-P_c^2$, is consistent with the many absences noted on Weissenberg photographs of the reciprocal lattice layers $h0l$, $h1l$, $h2l$, $hk0$ and $0kl$. No reflections were observed which required any other space group for the crystals.

The Structure Determination.—The intensities of the $h0l$, $0kl$ and $hk0$ reflections were visually estimated from Weissenberg photographs taken with unfiltered copper K radiation. In addition Weissenberg photographs of the $h0l$ reflections were taken using filtered molybdenum K radiation.

No corrections were made for absorption or extinction; the shape of the crystals (slightly elongated rhombohedra with b normal to the direction

TABLE I
X-RAY DATA FOR NICKEL GLYCINE DIHYDRATE OBTAINED WITH COPPER RADIATION

<i>hkl</i>	$ F_{est.} $	$F'_{calcd.}$	<i>hkl</i>	$ F_{est.} $	$F'_{calcd.}$	<i>hkl</i>	$ F_{est.} $	$F'_{calcd.}$	<i>hkl</i>	$ F_{est.} $	$F'_{calcd.}$	<i>hkl</i>	$ F_{est.} $	$F'_{calcd.}$
002	27.8	30.4	044	25.3	22.8	1.0 $\bar{1}0$	<3.6	-2.5	50 $\bar{4}$	<5.6	0.1	250	7.1	-8.2
004	36.6	44.2	045	<6.1	-4.9	200	9.7	-9.2	50 $\bar{6}$	15.8	21.2	260	8.3	1.5
006	25.0	21.4	046	20.2	19.8	202	34.1	38.8	600	15.8	12.0	270	<5.3	-0.6
008	25.6	27.3	047	<6.0	-6.7	204	6.8	-2.6	602	16.3	9.6	280	4.7	3.7
0.0.10	17.2	16.8	048	10.3	10.9	206	<4.9	-2.9	604	35.0	45.0	310	6.1	2.5
011	31.1	33.2	049	<4.2	0.4	208	7.0	3.7	606	7.6	-10.3	320	31.3	38.6
012	28.9	36.8	051	16.7	18.9	2.0.10	16.3	14.7	608	8.3	6.0	330	20.2	18.9
013	41.3	64.5	052	7.8	6.4	20 $\bar{2}$	13.5	13.0	6.0.10	5.4	1.5	340	37.4	47.8
014	22.4	20.0	053	30.2	35.0	20 $\bar{4}$	16.4	9.5	60 $\bar{2}$	12.8	9.3	350	11.7	-11.5
015	29.7	33.0	054	6.3	2.3	20 $\bar{6}$	20.0	18.7	60 $\bar{4}$	12.9	14.8	360	11.4	11.2
016	20.3	-16.9	055	15.6	15.0	20 $\bar{8}$	17.2	15.4	700	17.2	16.3	370	6.0	6.6
017	23.4	23.8	056	11.3	10.1	300	38.4	49.1	702	14.7	9.4	410	19.6	-20.0
018	8.3	8.4	057	17.9	17.9	302	43.4	56.5	704	32.8	40.1	420	32.1	35.9
019	13.9	13.3	058	<4.2	-2.2	304	32.4	39.6	706	24.3	29.7	430	13.8	13.8
0.1.10	6.5	6.0	060	26.3	26.0	306	24.5	23.4	708	11.0	9.7	440	21.1	22.8
020	25.2	32.6	061	7.9	6.2	308	6.7	4.6	7.0.10	14.0	14.3	450	13.9	-11.8
021	30.4	-33.1	062	6.3	3.8	3.0.10	14.3	15.5	70 $\bar{2}$	9.9	7.7	460	14.3	16.8
022	20.0	22.7	063	9.3	-5.5	3.0.12	7.1	5.9	800	6.5	5.7	470	4.3	4.7
023	4.7	5.5	064	17.9	19.0	30 $\bar{2}$	30.2	31.8	802	5.7	2.4	510	18.5	-15.6
024	36.6	55.6	065	<5.6	6.6	30 $\bar{4}$	26.0	24.3	804	13.5	10.1	520	18.2	14.4
025	<5.1	1.7	066	11.3	12.6	30 $\bar{6}$	21.7	20.4	806	19.3	20.6	530	7.1	-4.4
026	27.7	30.4	067	<3.9	3.8	30 $\bar{8}$	13.5	11.6	808	10.6	11.7	540	<5.8	-2.9
027	8.9	9.0	071	15.8	11.2	400	25.4	22.3	8.0.10	7.9	5.1	550	5.4	5.1
028	12.2	10.6	072	6.0	-2.5	402	42.1	69.4	902	3.5	1.7	560	10.8	9.1
029	<5.6	-2.9	073	14.6	11.8	404	21.8	20.5	904	7.9	5.6	570	<2.1	-3.7
0.2.10	13.8	17.6	074	<4.7	-2.3	406	33.6	45.5	906	9.3	4.6	610	10.7	-8.4
031	44.2	43.2	075	8.8	8.6	408	23.8	20.1	908	4.7	4.6	620	20.2	18.7
032	21.1	-20.8	080	19.5	22.4	4.0.10	21.5	22.6	110	21.4	-29.5	630	<5.7	-1.9
033	35.9	40.1	081	<3.9	2.6	4.0.12	16.5	15.5	120	8.1	7.6	640	15.2	13.3
034	5.1	-3.0	082	5.0	6.0	40 $\bar{2}$	24.2	18.2	130	12.8	14.9	650	9.6	9.0
035	<5.7	1.5	100	27.5	69.8	40 $\bar{4}$	14.0	9.9	140	16.7	15.7	660	<3.2	7.4
036	<6.1	-3.1	102	48.4	83.2	40 $\bar{6}$	12.5	13.3	150	13.9	-13.2	710	5.8	-2.8
037	31.7	38.4	104	7.9	0.7	500	9.5	-11.1	160	17.0	12.6	720	22.8	24.7
038	<5.8	2.1	106	31.0	29.5	502	28.8	33.6	170	<5.4	-1.4	730	6.5	4.4
039	11.3	11.1	108	20.9	18.0	504	16.3	12.7	180	9.5	9.9	740	9.2	9.6
0.3.10	<3.6	-5.9	1.0.10	27.0	29.4	506	6.8	-6.9	210	13.6	7.7	750	<2.7	-1.8
040	39.5	46.7	10 $\bar{2}$	25.4	-27.2	508	22.4	18.7	220	<3.6	3.2	810	6.3	7.5
041	18.8	14.4	10 $\bar{4}$	25.9	25.8	5.0.10	9.2	5.0	230	9.9	12.2	820	11.8	11.1
042	35.9	37.2	10 $\bar{6}$	<5.6	0.1	5.0.12	15.0	18.5	240	19.2	13.8	830	<3.3	-3.9
043	6.3	1.5	10 $\bar{8}$	22.2	25.3	50 $\bar{2}$	15.3	21.1						

of elongation) made an evaluation of the absorption corrections impractical. The crystals used had roughly the dimensions 0.2 mm. \times 0.4 mm. \times 0.5 mm.

Values of F^2 were obtained from the intensities estimated from the copper photographs by making the correction for the Lorentz and polarization factors. The values of F^2_{h0l} for reflections appearing only on photographs taken with molybdenum radiation were estimated by visual comparison with reflections, on the same film, which had previously been estimated on photographs taken with copper radiation. Appropriate corrections for the Lorentz and polarization factors were made. For example, if $I_{h0l} = I_{h'0l'}$ on a molybdenum photograph, and if F^2_{h0l} was known from a previous copper photograph, then it was assumed that $f(\theta_{h0l})F^2_{h0l} = f(\theta_{h'0l'})F^2_{h'0l'}$. Here $f(\theta)$ represents the angle-dependent Lorentz and polarization factors for the two reflections on the molybdenum photograph. The value of $F^2_{h'0l'}$ could then be found.

This procedure, while convenient, is not without error, because of the change in the atomic scattering factor for nickel in changing from copper to molybdenum K radiation. The presence of this

dispersion causes the F values to depend on λ as well as on $\sin \theta/\lambda$. The molybdenum data have therefore been placed in a separate table (Table II).

TABLE II
X-RAY DATA FOR NICKEL GLYCINE DIHYDRATE OBTAINED WITH MOLYBDENUM RADIATION

<i>h0l</i>	$ F_{est.} $	$F'_{calcd.}$	<i>h0l</i>	$ F_{est.} $	$F'_{calcd.}$
1.0.12	6.2	5.9	9.0.14	5.6	7.2
2.0.12	9.8	10.8	10.0.0	6.6	7.5
2.0. $\bar{1}2$	7.4	7.2	10.0.2	7.6	9.3
3.0.12	7.1	8.1	10.0.4	7.0	9.4
3.0. $\bar{1}0$	9.0	8.3	10.0.6	14.6	16.5
4.0.14	6.7	4.9	10.0.8	3.9	5.8
6.0.12	8.3	10.2	10.0.10	9.0	12.5
6.0. $\bar{6}$	15.2	16.0	11.0.2	5.6	8.2
7.0.12	14.4	13.8	11.0.6	9.8	14.4
7.0.14	10.5	11.4	11.0.8	5.9	7.9
7.0. $\bar{4}$	16.5	18.9	11.0.12	8.4	10.5
8.0.12	13.0	12.5	11.0.14	4.2	5.2
8.0.14	16.7	13.0	12.0.8	7.0	7.9
8.0. $\bar{4}$	7.0	9.6	13.0.8	5.6	7.0
9.0.0	9.1	10.7			

The Patterson projections $p(x,z)$, $p(x,y)$, and $p(y,z)$, appearing in Figs. 1, 4, and 7, respectively,

were calculated with use of the values of F_{h0l}^2 , F_{hk0}^2 and F_{0kl}^2 estimated from photographs made with copper radiation. In these figures a number of contours have been deleted around peaks corresponding to lattice translations. From an examination of the Patterson projections, parameters were assigned to the light atoms; the metal atoms were assigned to the special two-fold centrosymmetrical positions $(0,0,0)$ and $(0, \frac{1}{2}, \frac{1}{2})$.

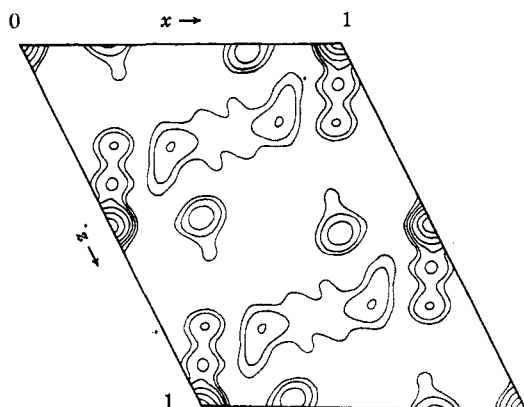


Fig. 1.—Patterson projection $p(x,z)$.

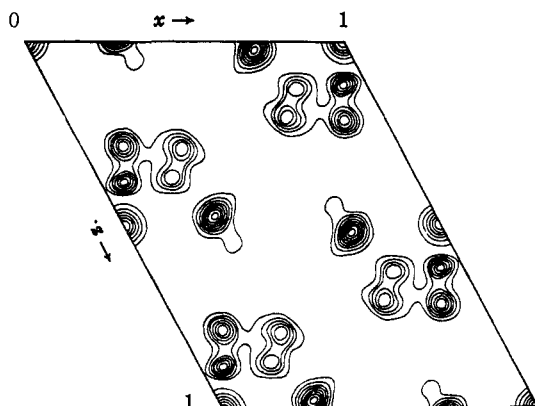


Fig. 2.—Fourier projection $\rho(x,z)$.

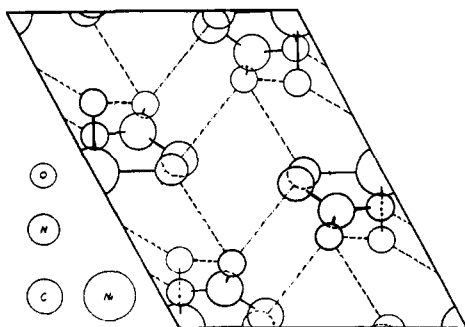


Fig. 3.—One unit cell of the structure as seen when observer is looking in the direction of the negative y axis. The x and z axes are oriented as they are in Fig. 2.

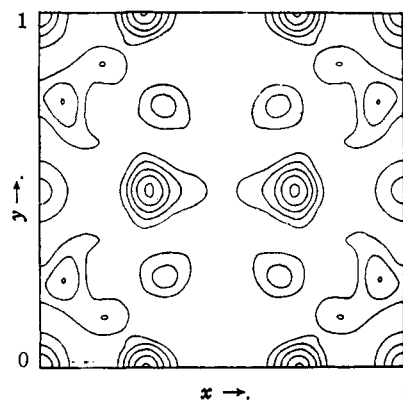


Fig. 4.—Patterson projection $p(x,y)$.

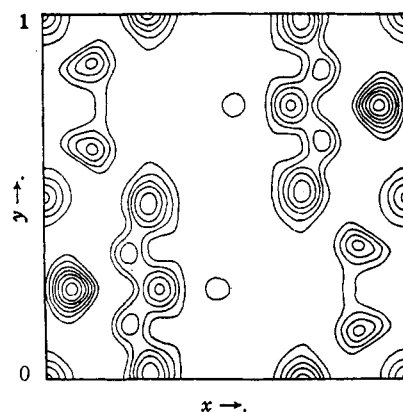


Fig. 5.—Fourier projection $\rho(x,y)$.

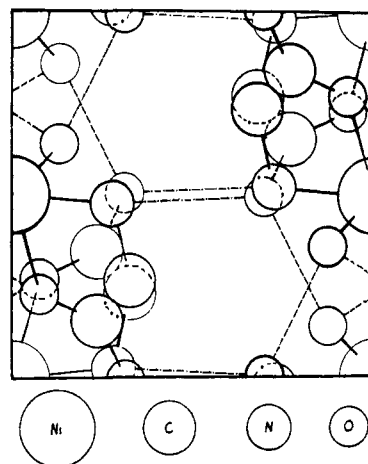
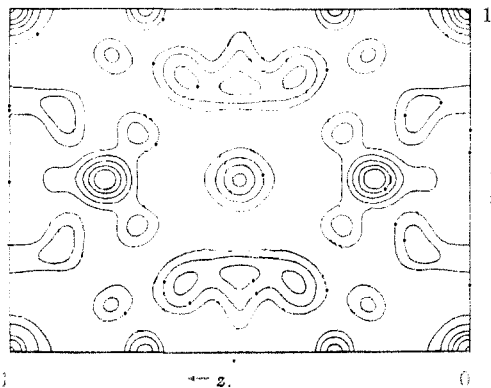
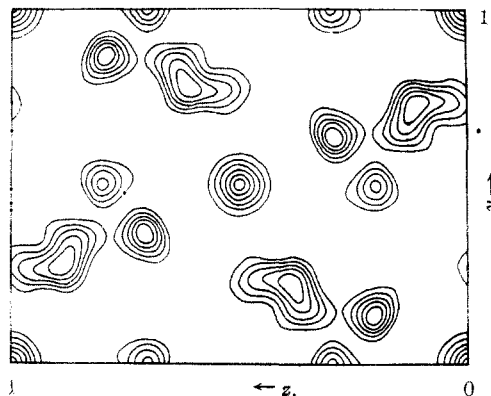


Fig. 6.—One unit cell of the structure projected on a plane normal to the z axis. Observer is looking in the direction of the negative z axis. The x and y axes are oriented as they are in Fig. 5.

Next the Fourier projections $\rho(x,z)$, $\rho(x,y)$, and $\rho(y,z)$ were calculated with use of F values estimated from the copper photographs and signs of the F 's from the best values available for the parameters at each stage of the calculations.

Fig. 7.—Patterson projection $\rho(y,z)$.Fig. 8.—Fourier projection $\rho(y,z)$.

Finally $\rho(x,z)$ was recalculated with use of the F values estimated from molybdenum photographs as well as those from the copper photographs. The second $\rho(x,z)$ projection is presented in Fig. 2, $\rho(x,y)$ and $\rho(y,z)$ appear in Figs. 5 and 8, respectively. In these figures only the zero level and positive contours are shown, and a number of contours have been omitted around the positions of the metal atoms.

The presence of the metal atoms at the centers of symmetry was an aid in the early part of the structure determination. In the Patterson projections peaks due to interatomic distance vectors between light atoms are much less important than peaks corresponding to interatomic distances involving a nickel atom. The Patterson projections, therefore, have many of the features of the corresponding Fourier projections and are easy to interpret.

For the $0kl$ reflections with $k + l = 2n$, for $hk0$ reflections with $k = 2n$, and for all of the $h0l$ reflections the nickel atoms contribute $+2f_{Ni}$ to the structure amplitude factor. In all but a few cases this term determines the sign of the corresponding F . The chance of having assigned wrong signs to these F 's is therefore very small.

By the same token the structure amplitude factors for these special classes of reflections are less sensitive to changes in the parameters of the light atoms, and it is correspondingly more difficult to refine the structure determination.

The Fourier and Patterson projections, except for the second $\rho(x,z)$ projection, were calculated with use of Beavers-Lipson strips having a tabular interval of $1/60$ of a cycle. The second $\rho(x,z)$ projection was calculated with equipment furnished to these laboratories by the International Business Machine Company, together with sets of punched cards for the trigonometric functions. The tabular interval in the punched-card calculation was $1/250$ of a cycle. The card file used in the calculation and the method of calculation are described in the Doctoral Dissertation of P. A. Shaffer, Jr.⁵

(5) P. A. Shaffer, Jr., Doctoral Dissertation, California Institute of Technology, 1942.

Because of the unfortunate orientation of the molecules with respect to the axes chosen for the crystal, the data at hand were not sufficient to determine all of the parameters for all of the light atoms from the projections. For example, the nitrogen atom is unresolved from other atoms on all of the projections for which calculations were made. The parameters which could not be determined from these projections were evaluated by placing the atoms in positions such that the interatomic distances assume reasonable values.

The value for the y parameter of O_1 was chosen so that the Ni-O distance is 2.08 Å. using the x and z parameters obtained for O_1 from the projections. The x parameter for the nitrogen atom was calculated from an assumed Ni-N distance of 2.09 Å. The y and z parameters of N have little effect on the Ni-N distance, since the Ni-N bond nearly coincides with the x axis. The value for the y parameter of C_2 , the α carbon atom, was calculated from an assumed C_1-C_2 distance of 1.50 Å. and the remaining parameters for C_1 and C_2 . The y parameter of the nitrogen atom was chosen such that the C_2-N distance became 1.42 Å. The z parameters of N and C_2 were determined from an attempted resolution of the N and C_2 peak on $\rho(x,z)$ with use of the previously determined value for x_N and x_{C_2} .

The parameters obtained are tabulated in Table III. From these parameters the values of

	Ni	O_1	O_2	O_3	N	C_1	C_2
x	0	0.074	0.308	0.132	0.276	0.232	0.322
y	0	.272	.505	.859	.025	.345	.233
z	0	.883	.790	.779	.996	.871	.959

F_{h0l} , F_{hk0} and F_{0kl} were calculated, with use of the atomic f values found in the "Internationale Tabellen."⁶ For those F 's observed with copper K radiation the atomic f value for nickel was decreased by 3.5 electron units. This value for the dispersion correction is in satisfactory agreement with spectrometric measurements on NiO made

(6) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1936.

by Wyckoff,⁷ and with the value calculated by Hönl⁸ from quantum mechanical considerations. No dispersion correction was made for those reflections estimated from molybdenum photographs.

From plots of $\log (F_{\text{calcd.}}/F_{\text{est.}})$ against $(\sin \theta/\lambda)^2$ the values of the scale factor k and of the coefficient a^2 of the exponential temperature factor were found for each zone. The averages of the three values for k and for a^2 were then used for all three zones. In Tables I and II the entries labeled $|F_{\text{est.}}|$ are the originally estimated values of $|F|$ multiplied by $k = 1.39$; the entries labeled $F'_{\text{calcd.}}$ are the values of $F_{\text{calcd.}} \exp. (-1.37 \sin^2\theta/\lambda^2)$. The agreement between $F'_{\text{calcd.}}$ and $F_{\text{est.}}$ (cf. Tables I and II) is moderately satisfactory, but undoubtedly could be further improved by refinement of the parameters.

Discussion of the Structure.—Figures 9, 3 and 6 are projections of the structure parallel to the x , y and z axes, respectively. Solid lines represent bonds within each of the molecules, and broken lines represent hydrogen bonds.

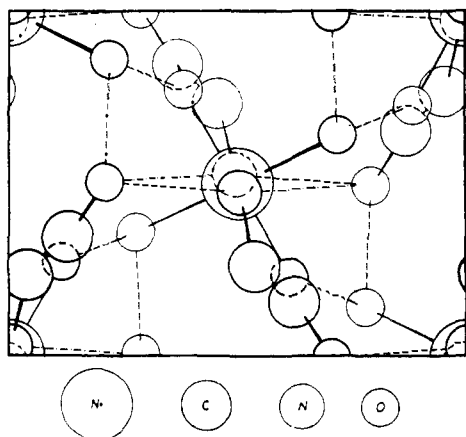


Fig. 9.—One unit cell of the structure projected on a plane normal to the x axis. Observer is looking in the direction of the negative x axis. The y and z axes are oriented as they are in Fig. 8.

The structure consists of distorted octahedral complexes of nickel atoms with two glycine residues and two water molecules. These complexes are bonded one to another by hydrogen bonds.

The nickel atom forms coplanar and nearly square covalent bonds to two oxygen atoms (2.08 Å., assumed) of carboxyl groups (O_1) and to two amino nitrogen atoms (2.09 Å., assumed). In addition the nickel atom forms covalent bonds to two oxygen atoms (2.12 Å.) of water molecules (O_3) at the remaining vertices of a distorted octahedron.

The calculated angles between various bonds in each complex are

(7) R. W. G. Wyckoff, *Phys. Rev.*, **35**, 583 (1930).

(8) (a) H. Hönl, *Ann. Physik*, **18**, 625 (1933). (b) Compton and Allison, "X-Rays in Theory and Experiment," D. Van Nostrand Company, Inc., New York, N. Y., 1935, p. 313.

$$\begin{aligned} O_1\text{-Ni-N} &= 84^\circ 1' \\ O_1\text{-Ni-O}_3 &= 86^\circ 46' \\ N\text{-Ni-O}_3 &= 89^\circ 46' \end{aligned}$$

Further bond distances and angles are shown in Fig. 10, which represents a view of a glycine residue as seen along a direction normal to the plane of $O_1\text{-O}_2\text{-C}_2$. The underscored numbers represent distances in ångström units above this plane.

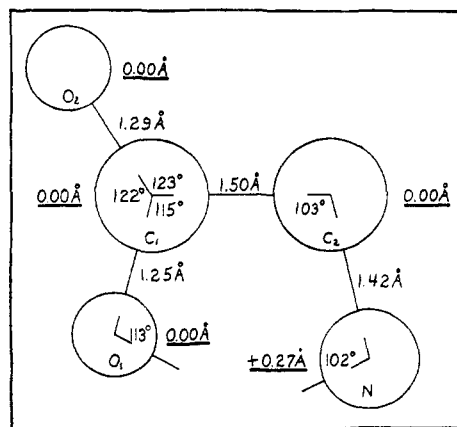


Fig. 10.—Glycine residue viewed along a direction normal to the plane of the carboxyl group oxygen atoms and the α -carbon atom.

Each of the water molecules (O_3) of a molecule of the octahedral complex forms two strong hydrogen bonds to oxygen atoms of two other molecules of the complex. The length of both of these hydrogen bonds is 2.72 Å. In addition the outer or carbonyl oxygen atoms (O_2) of the carboxyl groups form one strong and possibly a second weaker hydrogen bond to nitrogen atoms of the amino groups of other molecules. The O-N distances are 2.96 Å. and 3.13 Å., respectively. In the drawings (Figs. 3, 6 and 9) the longer O-N hydrogen bond is represented by the dot-dash lines. Thus each water molecule forms two strong hydrogen bonds to oxygen atoms, and each amino group forms two hydrogen bonds to carboxyl oxygen atoms, with one bond strong and the other weak. In the y and z directions the crystal is bonded together by strong hydrogen bonds, whereas in the x direction only the weak nitrogen-to-oxygen bonds are operative in addition to van der Waals forces.

The packing of the molecules along the x direction leads to the following reasonable values for the contact distances: NH_2 to NH_2 , 3.46 Å., CH_2 to NH_2 , 3.69 Å.

Acknowledgment.—The author wishes to acknowledge his indebtedness to Professor Linus Pauling for having suggested this problem and for his constructive criticism of the manuscript.

Summary

The crystal structure of nickel glycine dihydrate has been determined by X-ray methods.

The structure consists of slightly distorted octahedrally coordinated complexes of two glycine residues and two water molecules about the nickel atoms. These complexes are held to each other by strong oxygen-to-oxygen hydrogen bonds and by both strong and weak nitrogen-to-oxygen hydrogen bonds.

Because of the unfortunate orientation of the

molecule with respect to the axes of the crystal, some of the parameters were not evaluated from projections but were in part calculated from assumed interatomic distances.

The structure of the glycine residues is substantially the same as that found by Corey and Albrecht¹ for glycine.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LAFAYETTE COLLEGE]

The Diffusivities of Concentrated Sucrose Solutions¹

BY ANDREW VAN HOOK AND HARRY D. RUSSELL²

I. Introduction

Although dilute sucrose solutions are frequently employed as primary standards in diffusion studies, relatively little attention has been paid to the evaluation of this property at higher temperatures and at concentrations of the order of saturation. It is exactly these conditions at which the diffusivity is of much interest and value for the kinetic interpretation of the crystallization of sucrose.³ This paper reports the results of an endeavor to supply this desirable information.

II. Experimental and Results

The Northrup⁴-McBain⁵ porous disk technique was employed. Five different cells were employed, and each value presented in Fig. 1 is the average of at least two determinations in different cells. Solutions were analyzed refractometrically with a Bausch and Lomb dipping instrument, previously calibrated in almost perfect agreement with the values of the "International Sugar Tables."⁶ Weight percentages were computed to molarities, etc., by means of Plato's tables.⁶ Sucrose,⁷ potassium chloride⁷ and hydrochloric acid⁸ were used to calibrate the cells⁹ at temperatures below 35° while mannitol¹⁰ was used at higher temperatures. Excellent agreement was realized with these different standards.

The calibrated cell constant is essentially the ratio of the effective area of all pores to the thickness of the disk; and since the former will vary quadratically with the temperature and the latter changes only linearly, the net change of the cell constant will be a fractional increase of $\alpha \Delta t$, where α is the linear expansion coefficient of the glass of which the disk is constructed. α of Pyrex glass is of the order of 10^{-6} , which with the maximum temperature spread encountered in this work (80°) indicates an insignificant correction to the cell constant. Actually some slight increase in the cell constant is observed at increasing temperatures. Some values determined for some of the cells used in this work are presented in Table I. The values in parentheses were obtained when the cells were not previously well aged at the temperatures designated.

It was intended initially to investigate the diffusivities of supersaturated solutions in par-

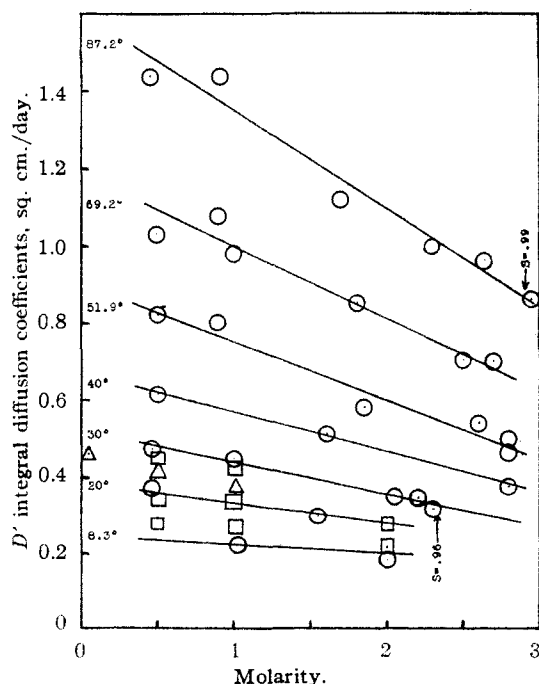


Fig. 1.—Integral diffusivities of sucrose solution: ○, this work; □, Ohlm, at 12, 20 and 29°, respectively, "I.C.T."; △, McBain,⁵ 25°.

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