

Mn, etc., as sulphates and B as borate) is necessary. The view that micronutrients should be supplied as "insurance" whether a need can be identified or not is gaining support among agronomists.

Considering the problem of uniform distribution of micronutrients in fertilizers, analysis of random batch samples for their trace element content could be adopted as one of the quality control measures in fertilizer industry.

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1. Kirk-Othmer, *Encyclopedia of Chemical Technology*, 2nd Completely Revised Edition, Interscience Publishers, 1966, 9, 25.
2. *Analytical Methods for Atomic Absorption Spectrophotometry*, Perkin-Elmer Corporation, Norwalk, Connecticut.
3. *Atomic Absorption Spectroscopy*, Juan Ramirez-Muñoz, Elsevier Publishing Company, 1968.
4. McBride, C. H., "Determination of minor nutrients in fertilizers by Atomic Absorption Spectrophotometry," *At. Absorption Newsletter*, 1964, 3, 11.
5. Billings, G. K., "Light scattering in trace element analysis by Atomic Absorption," *Ibid.*, 1965, 4, 10.
6. Hammar, H. E. and Page, N. R., "Micronutrient analysis of fertilizers with special reference to frits," *Ibid.*, 1967, 6, 2.

CRYSTAL STRUCTURES OF SOME ADDITION COMPOUNDS OF GLYCINE

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INTRODUCTION

It is well known that glycine forms addition compounds with many inorganic salts. Even though the structure of glycine itself has been analysed in detail¹⁻⁴ very little structural information is available about these addition compounds. Hence, it was felt worthwhile to carry out a systematic study of the crystal structures of some of them to gather information regarding the orientation of the glycine units in its different compounds and also to elucidate the nature of the hydrogen bonds present.

This note describes the main features of the structure of glycine molecule in three addition compounds of glycine, viz., Diglycine barium chloride monohydrate, Diglycine strontium chloride trihydrate and Diglycine manganese chloride.

EXPERIMENTAL

The compounds were crystallised by slow evaporation of aqueous solution of glycine and the respective salt (barium chloride, strontium chloride and manganese chloride) in stoichiometric proportions. Morphological studies showed the crystals of barium and strontium compounds to belong to the orthorhombic system

while the manganese compound crystallised in the triclinic class.

Unit cell dimensions of the three crystals were determined from oscillation and Weissenberg photographs taken with CuK_α radiation. The space groups were deduced from the symmetry of and the systematic absences in the respective X-ray diffraction patterns. The crystal data for all the three compounds are given in Table I. The present values for the

TABLE I

Crystal group	Barium compound Orthorhombic	Strontium compound Orthorhombic	Manganese compound Triclinic
Space group	P_{bcn}	P_{bcn}	$P\bar{1}$
Cell parameters	a 8.302 Å	16.52 Å	4.971 Å
	b 14.810 Å	9.34 Å	7.920 Å
	c 9.324 Å	8.25 Å	6.976 Å
	α 90°	90°	107° 43'
	β 90°	90°	115° 06'
	γ 90°	90°	87°
Unit cell volume Å ³	1143.0	1261.0	234.6
Density (measured) gm./c.c.	2.2	1.90	1.94
Density (calculated) gm./c.c.	2.182	1.892	1.932
Molecules per unit cell	4	4	1

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Mn compound are more accurate than those reported earlier. The densities were measured by flotation method as reported earlier.^{5,6}

Intensities were recorded on multiple films using the equi-inclination Weissenberg technique. Complete 3-D data were collected for the layers

$Hkl, H = 0,1,2,3,4 \text{ and } 5 \}$ for barium
 $hkL, L = 0,1,2,3,4 \text{ and } 5 \}$ compound,

and $Hkl \dots H = 0,1,2,3,4 \text{ and } 5 \}$ for strontium
 $hKl \dots K = 0,1,2,3,4 \text{ and } 5 \}$ compound

and $hkL \dots L = 0,1,2,3 \text{ and } 4 \}$ for manganese
 $Hkl \dots H = 0,1,2,3 \text{ and } 4 \}$ compound.

Intensities were measured by visual estimation against standard intensity strips recorded for the same crystals. The Lorentz, polarisation and absorption corrections were applied to the measured intensities and they were placed on an absolute scale using Wilson's procedure.

STRUCTURE DETERMINATION

All three structures have been determined by the heavy atom method. The first two structures (Ba and Sr compounds) are orthorhombic with space group P_{bcn} and contain four molecules in the unit cell whereas the last one (Mn compound) is triclinic with space group P_1 and contains only one molecule in the unit cell.

1. Ba Compound

Interpretation of the (hko) and (okl) Patterson projections enabled the Ba atom to be fixed with certainty. The position of Ba was then refined by the method of least squares. From the final structure factors, phases for many reflections could be deduced with certainty. Then a Ba removed difference Fourier showed clearly the chlorine position which was then refined. By successive application of difference synthesis and structure factor calculation and also by using a wire model of the glycine molecule according to Marsh's⁷ values, all the atoms of glycine could be located as also the water oxygen. With these atomic co-ordinates, 3-D data with 557 reflections were fed and a few cycles of least squares refinement were performed and the R-factor came down to 11.6%. The structure was still more refined giving anisotropic temperature factors and the R-factor was reduced to 8.6%.

2. Sr Compound

Sr compound crystallises with space group P_{bcn} but is not isomorphous with the Ba compound.

After locating the Sr atom from (hol) and (okl) Patterson maps, a few successive Fourier and difference Fourier syntheses enabled to locate all the atoms. The R-factor at this stage was 19%. Further refinement was done with 3-D data. With inclusion of anisotropic temperature factors, the R-factor came down to 7%.

3. Mn Compound

Mn compound crystallises in the triclinic system in which the possible space groups are P_1 and P_1 . Intensity statistics performed with an overall temperature factor of $B = 0.956 \text{ \AA}^2$ favours a centric structure. This is also to be expected from other considerations. The crystal was therefore assigned to space group P_1 .

It is obvious that Mn occupies the origin $(0,0,0)$. By the same procedure of iterative difference syntheses, all the atoms could be located. This gave an R-factor of 22.5%. When anisotropic temperature factors were included, a few cycles of least squares refinement brought down the R-factor to 10.8%.

To improve the accuracy of intensity measurements in order to draw more refined structural conclusions the intensities or reflections in all the three crystals were also measured using a Siemens 3-circle automatic single crystal diffractometer. This was made available to one of the authors (P.N.) through the kind courtesy of Prof. W. Hoppe of the Max Planck Institute to whom the authors thanks are due.

MAIN FEATURES OF THE STRUCTURES

From the results it is observed that the glycine molecule is in zwitter ion form in all the three cases. The molecular form of the glycine molecule is almost the same in all the structures. The molecule is planar except for the nitrogen atom which deviates from the planarity by 0.158 Å in the Ba compound, 0.141 Å in the Sr compound and 0.703 Å in the Mn compound. Table II gives the values for

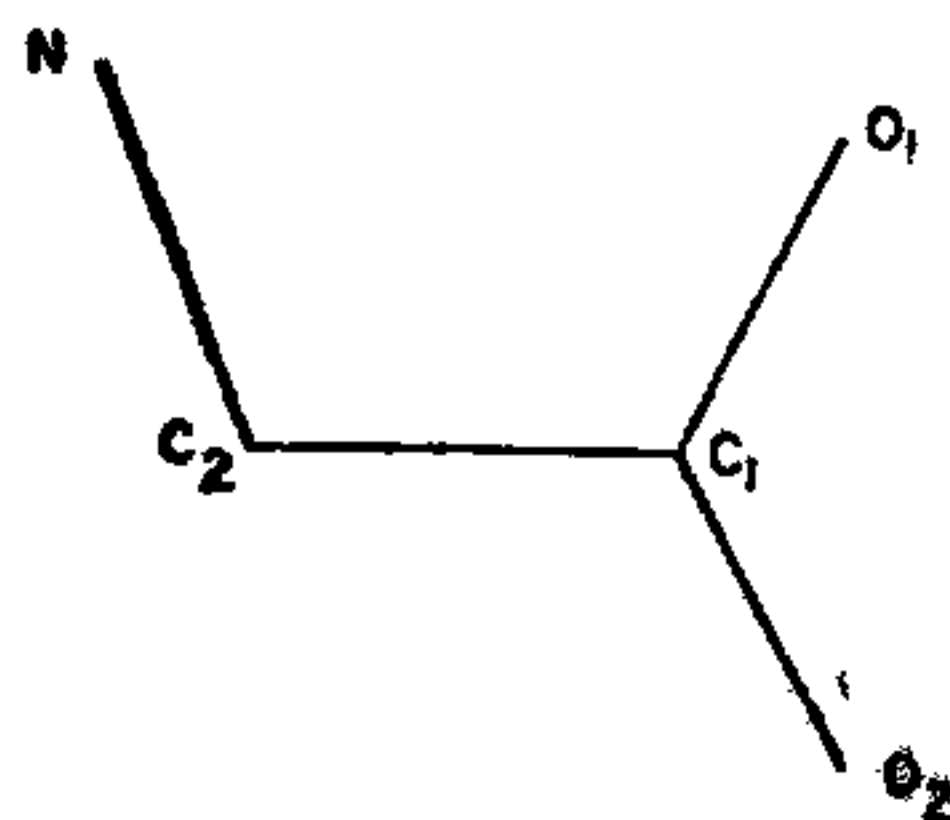


FIG. 1

TABLE II

Bond	Ba com- pound	Mn com- pound	Marsh α- glycine	Stosi k Ni gly dihydrate
	Å	Å	Å	Å
C ₁ -O ₁	1.293	1.248	1.254	1.25
C ₁ -O ₂	1.172	1.247	1.278	1.29
C ₁ -C ₂	1.526	1.519	1.512	1.50
C ₂ -N	1.507	1.481	1.508	1.42
Bond angles				
O ₁ -C ₁ -O ₂	124°·2	124°·2	124°·8	125°·5
O ₁ -C ₁ -C ₂	119°·8	119°·4	119°·5	117°·4
O ₂ -C ₁ -C ₂	116°·0	116°·4	115°·7	117°·1
C ₁ -C ₂ -N	111°·7	111°·5	110°·5	111°·8

the bond lengths and bond angles in the glycine molecule as revealed from the three structures as compared with those got for α-glycine by Marsh⁷ and for Nickel Glycine

dihydrate by Stosick.⁸ The structures seem to be stabilised by a set of hydrogen bonds.

Details of the structure will be published in due course after completing the refinement with diffractometer data.

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1. Albrecht, G. and Corey, R. B., *J. Am. Chem. Soc.*, 1939, **61**, 1087.
2. Kitaigorodsky, A., *Act. Physicochim. U.R.S.S.*, 1936, **5**, 749.
3. Ksanda, C. J. and Tunnell, G., *Am. J. Sci.*, 1936, **35 A**, 173.
4. Iitaka, Y., *Act. Cryst.*, 1958, **11**, 225.
5. Narayanan, P. and Shanta Venkata Raman, *Curr. Sci.*, 1967, **36**, 315.
6. — and —, *Z. Kristallogr.*, 1967, **124**, 460.
7. Marsh, R. E., *Act. Cryst.*, 1958, **11**, 654.
8. Stosick, A. J., *J. Am. Chem. Soc.*, 1945, **67**, 365.

EFFECTS OF PHOTOPERIODISM ON MOULTING IN *HEMIGRAPSPUS NUDUS* DANA

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ABSTRACT

In the shore crab, *Hemigrapsus nudus*, light as an environmental regulator of moulting is considered. Absence of light inhibits proecdysis, though increased light conditions do not accelerate it.

INTRODUCTION

LIGHT intensity and periodicity are known to influence crustacean moulting. There is evidence that moulting will be inhibited for several months in *Gecarcinus* if it is subjected to constant illumination (Bliss, 1954), but that darkness would favour its proecdysial growth (Bliss, 1964). *Cambarus* responds to daily photoperiod by an increased tendency to moult in winter months (Stephens, 1955). In *Carcinus* constant illumination retards moulting without affecting the duration of proecdysis (Passano, 1963). Kurup (1963) observed that, in *Hemigrapsus*, continuous illumination is not favourable for moult preparation, though pro-

longed darkness blocks moulting altogether. Controlled experiments, reported here, have further shown that moult responses of this shore crab, exposed to photoperiod, are considerably varied.

MATERIAL AND METHOD

Specimens of *Hemigrapsus nudus*, collected from Cape Arago, Oregon, U.S.A. were kept in aquarium tanks (2½' × 2' × 1½') containing sandbeds with sea-water. The tanks were continually aerated and were supported on black-painted metal jackets of constant-running freshwater to simulate tide-pool conditions. A thermostat was also suitably installed to maintain a temperature range of 13–15° C. in the tanks. The water jackets were also pro-

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