

## Crystal Structure of Glycine Silver(I) Nitrate

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(Received 11 August 1971 and in revised form 19 October 1971)

The crystal structure of glycine silver(I) nitrate,  $\text{NH}_2\text{CH}_2\text{COOH} \cdot \text{AgNO}_3$ , has been solved in the non-ferroelectric phase by the heavy-atom technique and refined to an  $R$  value of about 11% with four sets of intensity data, three sets collected at room temperature and one at  $-135^\circ\text{C}$ . The particular crystal with which the low temperature data were collected was found to have the space group  $P2_1/a$  although the reported ferroelectric transition to  $P2_1$  is at  $-55^\circ\text{C}$ . The crystals are monoclinic with four molecules in a unit cell of dimensions  $a=5.451$  (4),  $b=19.493$  (10),  $c=5.441$  (8) Å and  $\beta=100^\circ 12'(15')$  at room temperature, with space group  $P2_1/a$ . The silver atoms related centrosymmetrically are separated by a distance of 2.88 Å, the distance found in metallic silver. They bridge centrosymmetrical pairs of carboxyl groups forming dimers of glycines. The glycines in the structure exist as zwitterions,  $\text{NH}_3^+\text{CH}_2\text{COO}^-$ , the nitrogen atom being displaced from the mean plane of the  $\alpha$ -carbon atom and the carboxyl group by 0.33 Å. The glycine nitrogen atom forms three  $\text{N-H} \cdots \text{O}$  bonds with non-equivalent nitrate oxygens at less than 3 Å distance. The silver atoms are likely to play the most significant role in the ferroelectric transition of this crystal.

### Introduction

Pepinsky, Okaya, Eastman & Mitsui (1957) discovered that glycine silver(I) nitrate,  $\text{NH}_2\text{CH}_2\text{COOH} \cdot \text{AgNO}_3$  (abbreviated hereafter as GSN), was ferroelectric below  $-55^\circ\text{C}$ . This was the first crystal containing either silver or the nitrate ion in which ferroelectricity was observed. GSN has a spontaneous polarization,  $P_s$ , of 0.55 microCoulomb. $\text{cm}^{-2}$  at  $-195^\circ\text{C}$ . On partial substitution of silver by lithium or thallium, the Curie point is raised by about  $15^\circ\text{C}$  (Pepinsky, Vedam & Okaya, 1958; Pepinsky, Vedam, Hoshino & Okaya, 1958). This crystal has the point group symmetry  $2/m$  at room temperature and 2 in the ferroelectric phase. From the nature of  $P_s$  vs.  $T$  curve, it was concluded by Pepinsky and his colleagues that the transition was of the second order. However, no specific heat anomaly was observed by them. Mitani (1964) carried out dielectric measurements as well as lattice deformations from an X-ray study.

In the authors' laboratory, considerable research on various aspects of GSN has been in progress in recent years. Warriar & Narayanan (1967; see also Narayanan & Warriar, 1967) have recorded the infrared spectra of this compound and Easwaran (1966) the p.m.r. spectrum of a polycrystalline specimen. Tiwary, Devanarayanan & Narayanan (1969) measured the thermal expansion coefficient along the  $b$  axis using the Fizeau interferometric technique. The crystal structure analysis of GSN was taken up in view of these interests. A preliminary report of the structure has already appeared (Mohana Rao, 1968).

### Crystal growth

Crystals of GSN, of both acicular and platy habit, are grown in the dark by the evaporation of an aqueous solution containing stoichiometric amounts of glycine and silver nitrate. The crystals are normally transparent and colourless, but change their colour progressively from brown to black when exposed to light and X-rays.

They are very soft and plastic, tending to crumble on application of even a light touch. There are very good cleavage planes perpendicular to the  $a$  and  $b$  axes. The crystals can also be easily bent about the (010) plane. Because of the extreme plasticity of crystals, very few samples could survive cutting and grinding in general. Also, some of the crystals got damaged even after a few hours of exposure to X-rays while some others could withstand prolonged X-ray dosages.

### Crystal data

Glycine silver nitrate (GSN)  $\text{NH}_2\text{CH}_2\text{COOH} \cdot \text{AgNO}_3$ .  
Forms present: clinopinacoids {010}; prisms {110}, {120} and {130}; clinodomes {021}.

Formula weight 249.96

Melting point  $145^\circ\text{C}$

Transition temperature  $-55^\circ\text{C}$

At room temperature:

$a$  5.451 (4) Å

$b$  19.493 (10)

$c$  5.441 (8)

$\beta$   $100.2$  (0.25) $^\circ$

$V$   $579.5$  Å $^3$

Observed density  $2.79$  (3)  $\text{g.cm}^{-3}$

Calculated density 2.806

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Number of molecules in the unit cell = 4  
 Linear absorption coefficient ( $\lambda = 1.5418 \text{ \AA}$ ):  $290.3 \text{ cm}^{-1}$   
 Number of electrons in the unit cell: 472  
 Systematic absences at room temperature:  
 $h0l$ :  $h = 2n + 1$   
 $0k0$ :  $k = 2n + 1$   
 Space group =  $P2_1/a$ .

#### Intensity data at room temperature and at $-135^\circ\text{C}$

The complete structure analysis of GSN involved the use of data from six different crystals, one set of data being at  $-135^\circ\text{C}$  as given in Table 1. The data were collected by the multiple-film equi-inclination Weissenberg procedure using Ilford, Agfa or Indu films, depending on the availability of the particular brand of film. The crystals 5 and 6 were nearly 8 mm long.

Data were collected from these by feeding into the X-ray beam fresh regions of the crystals once in every 200 hours of exposure (the exposure time for each layer was approximately 70–100 hours). Thus it was possible to collect the complete  $hkL$  data from each of these crystals, the effect of radiation damage on X-ray intensities being reduced at the same time to the minimum. The intensities were visually estimated with a time-exposure calibrated strip and corrected for absorption and Lorentz-polarization factors as well as for spot shape in the upper layer Weissenberg pictures (Phillips, 1954) using a program written by Kannan (1965). Data obtained about different axes were put on the same relative scale by comparison of the reflections common to  $hkl$  and  $0kL$  Weissenberg pictures.

The cryostat used for work at low temperatures was the one designed earlier by Viswamitra & Kannan

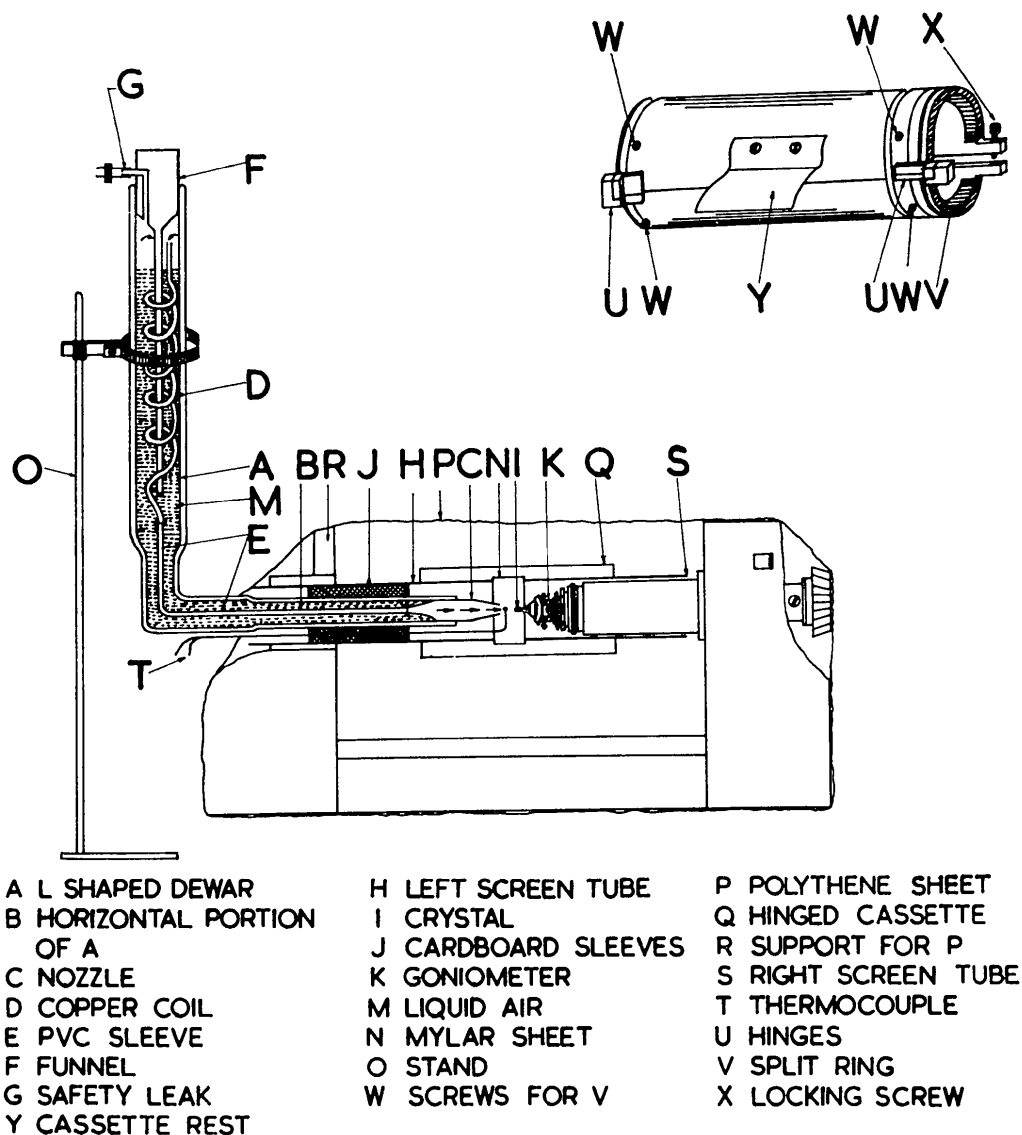


Fig. 1. Schematic diagram of the low temperature set-up.

(1962) in the authors' laboratory. A schematic diagram of the low temperature set-up is given in Fig. 1. The cylindrical film cassette (Fig. 1 top right) is split and hinged on one side so that it can be opened and slipped over the screen tubes without disturbing in any way the low temperature set-up (Viswamitra, 1971).

### Twinning

The crystals 5 and 6 (see Table 1) were found twinned in such a way that the two sets of spots from the twins overlapped completely in the  $hk3$  layer. In all the other layers, the intensities due to the twin components were clearly separated. Of the two sets of separated spots, one was stronger than the other, the average ratio (called the twinning ratio) of the stronger to the weaker being about 6.5 and 29.0 respectively for the fifth and sixth crystals. The overlap of spots in the third layer was such that  $0k3$  reflections coincided with the  $\bar{1}k3$  reflections,  $1k3$  with  $2k3$  etc., because the twin pairs of reflexions  $hk3$  and  $\bar{h}+1, k, 3$  had practically the same  $\sin^2 \theta$  values.

To evaluate the separate intensities of the overlapping pair from their composite intensities in the third layer, the following procedure was adopted. If  $I_1$  and  $I_2$  are the true intensities of the  $hk3$  and  $\bar{h}+1, k, 3$  reflexions and  $I'_1$  and  $I'_2$  are the measured intensities of reflexions 'indexed' as  $hk3$  and  $\bar{h}+1, k, 3$  then

$$(1+x)I'_1 = I_1 + xI_2 \quad \text{and} \quad (1+x)I'_2 = I_2 + xI_1. \quad (1)$$

Rearranging, we get

$$I_1 = \frac{(1+x)(I'_1 - xI'_2)}{(1-x^2)} \quad \text{and} \quad I_2 = \frac{(1+x)(I'_2 - xI'_1)}{(1-x^2)} \quad (2)$$

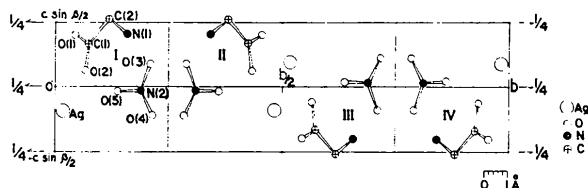


Fig. 2. The structure as viewed down the  $a$  axis. The equivalent positions are represented as follows:

$$\begin{array}{ll} \text{I} & x, y, z. \\ \text{II} & \frac{1}{2} + x, \frac{1}{2} - y, z. \\ \text{III} & \frac{1}{2} - x, \frac{1}{2} + y, -z \\ \text{IV} & -x, -y + 1, -z. \end{array}$$

where  $x$  is the reciprocal of the twinning ratio. The procedure given here is the same as that given by Grainger (1969) independently.

### Structure determination and refinement

Initially, the structure was solved by the use of data collected with crystals 1 and 2. The silver position was first obtained at  $(18/120, 2/120, -21/120)$  from the  $hk0$  and  $0kl$  projection Patterson syntheses. The rest of the structure was obtained from a three-dimensional Fourier synthesis based on the phases of silver with 358 coefficients.

For the purpose of refinement, the data from crystals 2, 3 and 4 were combined and these are designated as set 1. The data, later collected with crystals 5 and 6 at room temperature, designated as sets 2 and 3, were refined separately. Set 4 corresponds to the low temperature data with crystal 5. The space group for all these sets of data is  $P2_1/a$ .

Table 1. Details of the data collected using the various crystals of GSN

Crystal No.	Layers collected	No. of reflexions recorded	Mean radius of the crystal $r$	$\mu r$
1	$hkL$ ( $l=0$ to 3)	456	0.0065 cm	1.91
2	$0kL$	66	0.0073	2.15
3	$hkL$ ( $l=0$ to 3)	398	0.0072	2.09
4	$hkL$ ( $l=0$ to 5)	776	0.0211	6.13
5	$hkL$ ( $l=0$ to 5)	646	0.0031	0.90
	at room temperature	658		
6	$hkL$ ( $l=0$ to 5)	812	0.0050	1.45
	at $-135^\circ\text{C}$			

Table 2. Results of the refinement in the final cycle

	Set 1	Set 2	Set 3	Set 4 L.T.
No. of reflexions used in the refinement	825	627	799	631
$R$ value for all the atoms	0.111	0.114	0.111	0.125
$R$ value for silver atom alone	0.239	0.258	0.244	0.257
Maximum value of $\Delta/\sigma$	0.83	4.55	0.54	2.83
Average value of $\Delta/\sigma$	0.11	0.65	0.09	0.68
Minimum value of $\Delta/\sigma$	0.00	0.01	0.00	0.01
Total no. of reflexions	854	651	817	658
$R$ value for all the atoms	0.125	0.126	0.119	0.140
$R$ value for silver atom alone	0.244	0.262	0.248	0.258

The refinement was carried out on a CDC 3600 computer for all four sets of data using the program *LALS* written by Gantzel, Sparks & Trueblood. The weighting scheme due to Cruickshank

$$w = 1 / (a + |kF_o| + c|kF_o|^2 + d|kF_o|^3) \quad (3)$$

was used with  $a = 20.0$ ,  $c = 0.0133$ ,  $d = 0.00025$ ,  $k = 1.0$ . The refinement in the initial stages was carried out isotropically using full matrix, and later anisotropically in diagonal approximation. The anisotropic thermal parameters were of the form

$$T = \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl). \quad (4)$$

Considerable discrepancy was observed between the  $F_o$  and  $F_c$  values of a few reflexions in each set of data. These were omitted in the final refinement. Refinement was stopped when the shifts were less than the standard

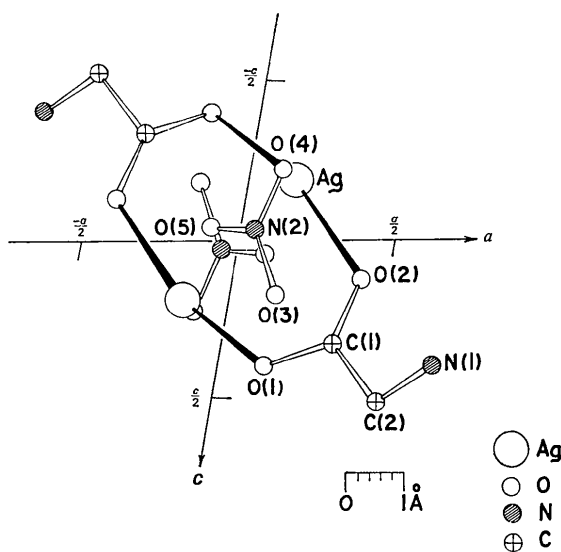


Fig. 3. A view along the [010] direction, showing the existence of glycine-dimers bridged by silver atoms. All the labelled atoms have the coordinates  $(x, y, z)$ .

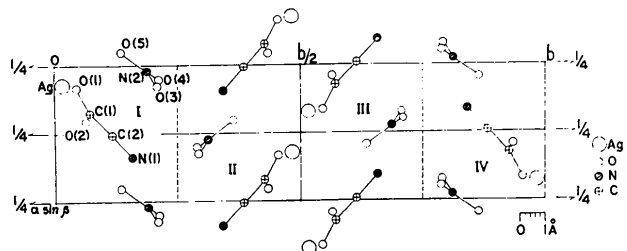


Fig. 4. The contents of the unit cell when viewed along the  $c$  axis. The asymmetric units have the following code:

- I  $x, y, z.$
- II  $\frac{1}{2} + x, \frac{1}{2} - y, z.$
- III  $\frac{1}{2} - x, \frac{1}{2} + y, -z.$
- IV  $-x + 1, -y + 1, -z.$

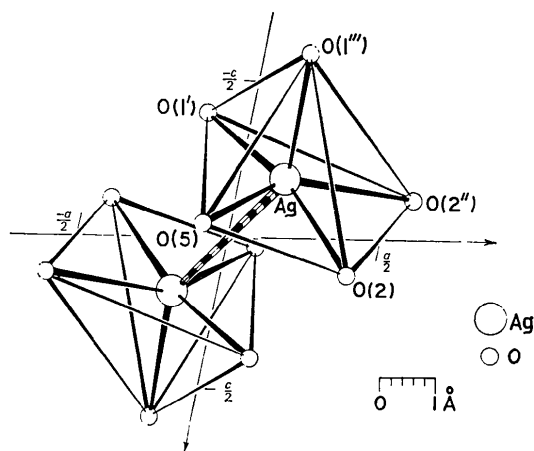


Fig. 5. The surroundings of the silver atoms related by the inversion centre at  $(0,0,0)$ . The Ag-O bond is represented by thick, partially shaded lines. The labelled atoms have the following coordinates:

- O(2), O(5), Ag  $x, y, z.$
- O(1')  $-x, -y, -z.$
- O(2'')  $-x + 1, -y, -z.$
- O(1''')  $x, y, z - 1.$

deviations. The results of the refinement in the final cycle are given in Table 2.

The scattering factors for the silver ion as well as the oxygen, nitrogen and carbon atoms were those given by Cromer & Waber (1965). The  $Ag^+$  form factors were corrected for dispersion with the  $\Delta f'$  term added on to the real part of the form factors already obtained. The angular dependence of  $\Delta f''$  was not taken into account.

### Results

The positions of the atoms in the asymmetric part of the unit cell and their thermal parameters are given in Table 3. The anisotropic thermal parameters from the different sets of data are widely different and they are not accurate enough to merit any discussion. However, it can be seen from Table 3(b) that the average  $B$  values obtained from low temperature data are, in general, half as large as those obtained at room temperature, indicating a significant reduction of thermal vibrations on cooling. Table 3(a) also gives the peak heights at the atomic sites and their standard deviations. These standard deviations were calculated by the use of the (Cruickshank, 1965) formula:

$$\sigma^2[\rho(xyz)] = (1/V^2) \left[ \sum_{indep} \{ \sigma^2(F) \left( \sum_{form} \cos \theta \right)^2 \} \right] \quad (5)$$

where  $\sigma(F)$  was taken as  $||F_o| - |F_c||$ . These were calculated using a program written by one of the authors (J.K.M.R.) in *FORTRAN* for the space group  $P2_1/a$ . Figs. 2, 3 and 4 are three views of the structure looking down the  $a$ ,  $b$  and  $c$  axes.

In the following paragraphs, the distances and angles

Table 3. *Fractional coordinates, thermal parameters, and observed and calculated electron densities*

(a) Fractional coordinates of the atoms in the asymmetric part of the unit cell and the observed and calculated electron densities ( $e \cdot \text{\AA}^{-3}$ ) with their errors. The maximum standard deviation (from least-squares) and the maximum deviation from the mean value corresponding to the sets 1, 2 and 3 are also given.

		At room temperature			At low temperature	
		Mean value	Max. standard deviation	Max. deviation from the mean	Value	Standard deviation
Ag	<i>x</i>	0.1450	0.0004	0.0015	0.1437	0.0005
	<i>y</i>	0.01631	0.00010	0.00013	0.01663	0.00012
	<i>z</i>	-0.1855	0.0004	0.0007	-0.1852	0.0004
	$\rho_{\text{obs}}$	86.5	0.5	16.0	106.3	0.6
	$\rho_{\text{cal}}$	87.8		14.8	103.6	
O(1)	<i>x</i>	0.166	0.003	0.004	0.167	0.005
	<i>y</i>	0.0430	0.0009	0.0016	0.0394	0.0012
	<i>z</i>	0.401	0.003	0.003	0.408	0.004
	$\rho_{\text{obs}}$	10.2	0.4	0.7	15.4	0.6
	$\rho_{\text{cal}}$	10.2		0.6	14.0	
O(2)	<i>x</i>	0.412	0.003	0.000	0.419	0.004
	<i>y</i>	0.0645	0.0009	0.0015	0.0641	0.0012
	<i>z</i>	0.126	0.003	0.004	0.126	0.004
	$\rho_{\text{obs}}$	10.9	0.4	2.0	11.7	0.6
	$\rho_{\text{cal}}$	11.1		2.0	10.2	
O(3)	<i>x</i>	0.151	0.003	0.002	0.166	0.005
	<i>y</i>	0.2074	0.0010	0.0009	0.2092	0.0013
	<i>z</i>	0.180	0.004	0.001	0.173	0.005
	$\rho_{\text{obs}}$	10.4	0.4	0.1	11.2	0.6
	$\rho_{\text{cal}}$	10.7		0.3	10.6	
O(4)	<i>x</i>	0.103	0.005	0.004	0.115	0.005
	<i>y</i>	0.2124	0.0013	0.0020	0.2129	0.0012
	<i>z</i>	-0.222	0.005	0.004	-0.227	0.004
	$\rho_{\text{obs}}$	6.7	0.5	1.9	9.0	0.6
	$\rho_{\text{cal}}$	6.9		1.8	8.2	
O(5)	<i>x</i>	-0.095	0.004	0.001	-0.094	0.004
	<i>y</i>	0.1360	0.0010	0.0004	0.1367	0.0009
	<i>z</i>	-0.038	0.004	0.004	-0.018	0.004
	$\rho_{\text{obs}}$	9.0	0.5	2.7	10.6	0.6
	$\rho_{\text{cal}}$	9.1		3.0	10.5	
N(1)	<i>x</i>	0.689	0.004	0.004	0.700	0.006
	<i>y</i>	0.1589	0.0011	0.0003	0.1571	0.0014
	<i>z</i>	0.403	0.005	0.002	0.408	0.005
	$\rho_{\text{obs}}$	8.3	0.4	2.7	8.4	0.6
	$\rho_{\text{cal}}$	8.5		2.6	7.9	
N(2)	<i>x</i>	0.047	0.004	0.004	0.069	0.005
	<i>y</i>	0.1884	0.0010	0.0025	0.1882	0.0013
	<i>z</i>	-0.030	0.004	0.005	-0.031	0.006
	$\rho_{\text{obs}}$	8.9	0.4	0.7	8.4	0.6
	$\rho_{\text{cal}}$	9.1		0.7	7.9	
C(1)	<i>x</i>	0.355	0.005	0.004	0.359	0.006
	<i>y</i>	0.0710	0.0012	0.0024	0.0698	0.0013
	<i>z</i>	0.333	0.005	0.002	0.340	0.005
	$\rho_{\text{obs}}$	7.2	0.4	2.0	7.5	0.6
	$\rho_{\text{cal}}$	7.7		2.1	7.4	
C(2)	<i>x</i>	0.516	0.005	0.007	0.525	0.005
	<i>y</i>	0.1166	0.0015	0.0008	0.1145	0.0014
	<i>z</i>	0.524	0.006	0.004	0.532	0.006
	$\rho_{\text{obs}}$	7.8	0.5	1.4	6.6	0.6
	$\rho_{\text{cal}}$	8.0		1.7	6.7	

Table 3(cont.)

(b) Anisotropic thermal parameters of the atoms in the asymmetric part of the unit cell. The temperature factor was of the form given in equation (4). The equivalent isotropic temperature factor,  $B(\text{\AA}^2)$ , was calculated using the Hamilton (1959) formula. The maximum standard deviation (from least-squares) as well as the maximum deviation from the mean value corresponding to the sets 1, 2 and 3 are also given.

		At room temperature		Max.	At low temperature	
		Mean	Max.	deviation	Value	Standard
		value	standard	from the		deviation
			deviation	mean		
Ag	$b_{11}$	0.0275	0.0006	0.0007	0.0184	0.0008
	$b_{22}$	0.00293	0.00004	0.00017	0.00180	0.00005
	$b_{33}$	0.0314	0.0006	0.0102	0.0094	0.0007
	$b_{12}$	-0.0061	0.0003	0.0008	-0.0020	0.0004
	$b_{13}$	0.0041	0.0011	0.0104	0.0151	0.0013
	$b_{23}$	-0.0035	0.0003	0.0002	-0.0011	0.0004
	$B$	3.8		0.4	1.9	
O(1)	$b_{11}$	0.029	0.006	0.007	0.039	0.011
	$b_{22}$	0.0032	0.0005	0.0006	0.0018	0.0005
	$b_{33}$	0.032	0.007	0.023	0.010	0.007
	$b_{12}$	-0.003	0.003	0.008	0.005	0.004
	$b_{13}$	-0.006	0.011	0.005	-0.004	0.015
	$b_{23}$	-0.004	0.003	0.012	-0.004	0.003
	$B$	4.2		0.9	2.8	
O(2)	$b_{11}$	0.021	0.005	0.005	0.022	0.008
	$b_{22}$	0.0027	0.005	0.0011	0.0025	0.0006
	$b_{33}$	0.032	0.006	0.001	0.010	0.007
	$b_{12}$	-0.001	0.003	0.007	0.002	0.004
	$b_{13}$	-0.004	0.009	0.022	0.004	0.014
	$b_{23}$	-0.003	0.003	0.003	-0.004	0.003
	$B$	3.5		0.2	2.5	
O(3)	$b_{11}$	0.035	0.007	0.007	0.021	0.009
	$b_{22}$	0.0030	0.0005	0.0008	0.0024	0.0006
	$b_{33}$	0.049	0.008	0.008	0.021	0.008
	$b_{12}$	0.004	0.003	0.002	0.000	0.004
	$b_{13}$	-0.022	0.012	0.032	0.016	0.015
	$b_{23}$	-0.006	0.003	0.001	-0.001	0.004
	$B$	5.0		0.5	2.7	
O(4)	$b_{11}$	0.043	0.011	0.013	0.043	0.012
	$b_{22}$	0.0053	0.0009	0.0014	0.0022	0.0006
	$b_{33}$	0.052	0.010	0.011	0.010	0.007
	$b_{12}$	-0.002	0.004	0.003	-0.003	0.005
	$b_{13}$	-0.001	0.018	0.011	0.002	0.016
	$b_{23}$	0.002	0.005	0.004	0.004	0.004
	$B$	6.5		0.5	3.2	
O(5)	$b_{11}$	0.040	0.008	0.012	0.017	0.007
	$b_{22}$	0.0021	0.0005	0.0004	0.0010	0.0004
	$b_{33}$	0.054	0.009	0.020	0.022	0.008
	$b_{12}$	-0.003	0.004	0.001	-0.002	0.003
	$b_{13}$	-0.018	0.015	0.002	0.018	0.013
	$b_{23}$	-0.003	0.004	0.004	-0.005	0.003
	$B$	5.0		1.2	1.9	
N(1)	$b_{11}$	0.030	0.007	0.005	0.030	0.011
	$b_{22}$	0.0021	0.0006	0.0010	0.0017	0.0007
	$b_{33}$	0.046	0.009	0.010	0.016	0.010
	$b_{12}$	-0.003	0.003	0.005	0.001	0.004
	$b_{13}$	-0.010	0.014	0.011	0.006	0.018
	$b_{23}$	0.005	0.004	0.003	0.003	0.004
	$B$	4.2		0.8	2.6	
N(2)	$b_{11}$	0.024	0.007	0.003	0.017	0.008
	$b_{22}$	0.0020	0.0005	0.0002	0.001	0.0005
	$b_{33}$	0.052	0.010	0.008	0.051	0.015
	$b_{12}$	0.001	0.003	0.004	-0.004	0.004
	$b_{13}$	-0.005	0.015	0.015	-0.011	0.020
	$b_{23}$	-0.002	0.003	0.005	0.006	0.005
	$B$	4.2		0.2	3.4	

Table 3 (cont.)

C(1)	$b_{11}$	0.036	0.009	0.021	0.021	0.011
	$b_{22}$	0.0013	0.0005	0.0006	0.0010	0.0006
	$b_{33}$	0.033	0.010	0.035	0.010	0.010
	$b_{12}$	-0.004	0.003	0.003	-0.003	0.004
	$b_{13}$	-0.036	0.014	0.053	0.012	0.018
	$b_{23}$	-0.001	0.004	0.003	0.003	0.004
	$B$	3.7		2.5	1.6	
C(2)	$b_{11}$	0.028	0.009	0.002	0.010	0.009
	$b_{22}$	0.0023	0.0008	0.0009	0.0016	0.0006
	$b_{33}$	0.034	0.013	0.032	0.010	0.009
	$b_{12}$	-0.007	0.004	0.002	0.004	0.004
	$b_{13}$	-0.014	0.019	0.006	0.010	0.016
	$b_{23}$	-0.006	0.005	0.003	-0.004	0.004
	$B$	3.8		1.7	1.5	

Table 4. Surroundings of the silver atom in the structure

The maximum standard deviation as well as the maximum deviation from the mean value corresponding to the data sets 1, 2 and 3 at room temperature are given with the values at low temperature.

	At room temperature		Max. deviation from the mean	At low temperature	
	Mean value	Max. standard deviation		Value	Standard deviation
Distances in Å					
Ag-O(1) (-x, -y, -z)	2.22	0.02	0.01	2.18	0.02
Ag-O(2)	2.25	0.02	0.01	2.26	0.02
Ag-O(1) (x, y, z-1)	2.37	0.02	0.02	2.32	0.02
Ag-O(2) (-x+1, -y, -z)	2.85	0.02	0.03	2.79	0.02
Ag-O(5)	2.86	0.02	0.01	2.89	0.02
Ag-Ag(-x, -y, -z)	2.877	0.006	0.014	2.849	0.007
Angles in degrees					
O(1) (-x, -y, -z)-Ag-O(2)	163.1	0.7	1.0	165.2	0.9
O(5)-Ag-O(2) (-x+1, -y, -z)	146.7	0.5	0.2	145.6	0.6
O(1) (x, y, z-1)-Ag-Ag(-x, -y, -z)	149.9	0.4	0.7	150.5	0.6
O(1) (-x, -y, -z)-Ag-O(5)	103.5	0.6	0.5	104.3	0.8
O(5)-Ag-O(2)	73.0	0.6	0.5	72.1	0.7
O(2)-Ag-O(2) (-x+1, -y, -z)	73.9	0.6	0.4	73.6	0.9
O(2) (-x+1, -y, -z)-Ag-O(1) (-x, -y, -z)	109.0	0.6	0.5	109.2	0.8
O(1) (x, y, z-1)-Ag-O(5)	101.5	0.6	1.3	105.1	0.7
O(5)-Ag-Ag(-x, -y, -z)	68.9	0.5	0.1	68.0	0.5
Ag(-x, -y, -z)-Ag-O(2) (-x+1, -y, -z)	110.9	0.4	0.8	109.8	0.5
O(2) (-x+1, -y, -z)-Ag-O(1) (x, y, z-1)	92.8	0.5	0.8	91.9	0.8
O(1) (-x, -y, -z)-Ag-O(1) (x, y, z-1)	76.0	0.7	0.4	73.2	1.1
O(1) (x, y, z-1)-Ag-O(2)	120.9	0.6	0.9	121.6	0.9
O(2)-Ag-Ag(-x, -y, -z)	84.7	0.4	0.6	84.7	0.7
Ag(-x, -y, -z)-Ag-O(1) (-x, -y, -z)	79.1	0.5	0.9	80.7	0.7
C(1)-O(2)-Ag	120.8	1.5	1.3	120.0	2.0
O(1)-C(1)-O(2)	124.9	2.3	1.9	124.9	2.6
Ag(-x, -y, -z)-O(1)-C(1)	130.0	1.7	0.8	128.7	2.0

quoted are the mean values obtained from the three sets of data 1, 2 and 3 collected at room temperature. These values are not significantly different from those obtained from the low temperature data (set 4).

#### Coordination of the silver atoms

The distances of the atoms close to the silver atom at less than 3 Å and the relevant angles are listed in Table 4. The two silver atoms, related by the inversion centre at the origin, are separated by a mean distance of 2.88 Å, the same as that found in metallic silver (2.889 Å; Wyckoff, 1965). They bridge the centro-

symmetrically related carboxyl groups, forming dimers of glycines as shown in Fig. 3. The silver atom is practically at the centre of the O(1) (-x, -y, -z)-Ag-O(2) bond (the Ag-O distances being 2.22 and 2.25) Å, which is slightly non-linear (O-Ag-O = 163°). Since the molecules exist as dimers because of silver bridging, the actual chemical formula of the compound is better represented by  $(\text{NH}_3^+\text{CH}_2\text{COO}^-\text{Ag}^+)_2(\text{NO}_3^-)_2$ . The whole group of atoms consisting of Ag, O(1), O(2), C(1) and C(2) and their centrosymmetrical equivalents is planar with the point group symmetry  $2/m$ .

The complete surroundings of the silver atoms are

shown in Fig. 5. Besides the closest oxygens at 2.22 and 2.25 Å, there is one more, O(1) ( $x, y, z-1$ ) at a distance of 2.37 Å from Ag. The four atoms [O(1) ( $x, y, z-1$ ), O(2), O(1) ( $-x, -y, -z$ ) and Ag] are coplanar and the silver coordination can be considered as triangular. The coordination polyhedron can be considered as a distorted octahedron if the next nearest neighbours *viz.* O(2) ( $-x+1, -y, -z$ ) (at 2.85 Å), O(5) (at 2.86 Å)

and Ag ( $-x, -y, -z$ ) (at 2.88 Å) are also taken into account.

Dimeric formation of carboxyl groups with short Ag-Ag contacts has also been found in the structure of silver perfluorobutyrate [Blackslee & Hoard, 1956; Ag-Ag=2.90 (2) Å, Ag-O=2.25 Å and O-Ag-O=160°]. In this structure also, the two silver atoms and the carboxyl groups are coplanar with point

Table 5. *Dimensions of glycine in GSN and other glycine compounds*

The standard deviations are given in parentheses.

## (a) Bond distances

Compound	C(1)-O(1) (Å)	C(1)-O(2) (Å)	C(1)-C(2) (Å)	C(2)-N(1) (Å)	N(1)-O(2) (Å)	Reference
GSN at room temperature	1.28 (3)	1.25 (3)	1.54 (4)	1.50 (4)	2.69 (3)*	<i>a</i>
at low temperature	1.30 (4)	1.28 (4)	1.53 (4)	1.50 (4)	2.67 (4)	
$\alpha$ -Glycine	1.25 (2) 1.255 (5) 1.265 (5)‡	1.27 (2) 1.252 (5) 1.261 (5)‡	1.52 (2) 1.523 (5)	1.39 (2) 1.474 (5)	2.690 (5)†	<i>b</i> <i>c</i>
$\beta$ -Glycine	1.25 1.257 (15)	1.24 1.233 (15)	1.52 1.521 (15)	1.48 1.484 (15)		<i>d</i> <i>e</i>
$\gamma$ -Glycine	1.22 1.237 (11)	1.29 1.254 (11)	1.53 1.527 (11)	1.46 1.491 (11)	2.687 (11)	<i>f</i> <i>g</i>
Diglycine hydrochloride	1.320 (30) 1.294 (30) 1.310 (10) 1.263 (10)	1.235 (30) 1.254 (30) 1.223 (10) 1.269 (10)	1.480 (30) 1.485 (30) 1.508 (10) 1.500 (10)	1.521 (30) 1.528 (30) 1.487 (10) 1.502 (10)	2.70 2.70	<i>h</i> <i>i</i>
Diglycine hydrobromide	1.29 1.22 1.30 1.225	1.25 1.24 1.225 1.255	1.52 1.50 1.505 1.53	1.52 1.56 1.535 1.52		<i>j</i> <i>k</i>
Diglycine nitrate at room temp.	1.257 (14) 1.288 (12)	1.225 (13) 1.244 (12)	1.527 (15) 1.492 (14)	1.503 (14) 1.482 (14)	2.705 (12) 2.673 (12)	<i>l</i>
at -150°C	1.278 (17) 1.285 (17)	1.236 (16) 1.232 (16)	1.528 (18) 1.536 (18)	1.466 (19) 1.456 (18)	2.709 (15) 2.663 (14)	
Triglycine sulphate	1.230 (40) 1.294 (40) 1.314 (40)	1.289 (40) 1.230 (40) 1.251 (40)	1.547 (40) 1.554 (40) 1.513 (40)	1.455 (40) 1.535 (40) 1.467 (40)	2.580 (40) 2.691 (40) 2.713 (40)	<i>m</i>
	1.230 1.294 1.314	1.289 1.230 1.211§	1.547 1.554 1.513	1.456§ 1.535 1.443§		
Copper glycine H <sub>2</sub> O	1.26 (5) 1.29 (5) 1.226 (15) 1.243 (15)	1.23 (5) 1.27 (5) 1.275 (14) 1.291 (15)	1.44 (6) 1.47 (6) 1.498 (17) 1.541 (18)	1.44 (6) 1.48 (6) 1.473 (16) 1.484 (17)	3.01 (4) 3.01 (4) 2.663 (14) 2.691 (16)	<i>n</i> <i>o</i>
Nickel glycine 2H <sub>2</sub> O	1.29 1.26 (1)	1.25 1.28 (1)	1.50 1.52 (1)	1.42 1.47 (1)		<i>p</i> <i>q</i>
Platinum glycine	1.231 (7)	1.290 (6)	1.510 (8)	1.496 (7)		<i>r</i>
Diglycine barium chloride H <sub>2</sub> O	1.172	1.293	1.526	1.507		<i>s</i>
Diglycine strontium chloride 3H <sub>2</sub> O	1.247	1.248	1.519	1.481		<i>s</i>
Diglycine manganous chloride	1.278	1.254	1.512	1.508		<i>s</i>
Cadmium glycine	1.29**	1.23**	1.58**	1.46**	2.93**	<i>t</i>



Table 5 (cont.)

(b) Bond angles and the deviation of the terminal nitrogen atom from the plane of the carboxyl group and the  $\alpha$ -carbon atom

Compounds	O(1)-C(1)-O(2) ( $^{\circ}$ )	O(1)-C(1)-C(2) ( $^{\circ}$ )	O(2)-C(1)-C(2) ( $^{\circ}$ )	C(1)-C(2)-N(1) ( $^{\circ}$ )	$\Delta$ (Å)	Reference
GSN at room temp.	125 (2)	116 (3)	119 (2)	110 (3)	0.33*	<i>a</i>
at low temp.	125 (3)	116 (3)	119 (3)	109 (3)	0.31	
$\alpha$ -Glycine	122 (3)	119 (3)	119 (3)	112 (3)	0.268	<i>b</i>
	125.5 (3)	117.1 (3)	117.4 (3)	111.8 (3)	0.436	<i>c</i>
$\beta$ -Glycine	126	116	118	111	0.59	<i>d</i>
	126.2 (9)	115.9 (9)	117.8 (9)	110.8 (9)	0.583	<i>e</i>
$\gamma$ -Glycine	122	114	122	107		<i>f</i>
	125.4 (7)	116.2 (7)	118.3 (7)	110.8 (7)	0.309	<i>g</i>
Diglycine hydrochloride	124.1 (7)	113.0 (7)	122.9 (7)	109.4 (7)	0.33	<i>h</i>
	124.4 (7)	116.1 (7)	119.5 (7)	112.0 (7)	0.04	
	124.7	113.3	122.2	110.2		<i>i</i>
	125.7	117.2	117.2	114.0		
Diglycine hydrobromide	128	121	112	111	0.49	<i>j</i>
	128	114	119	113	0.00	
	130	113	117	107		<i>k</i>
	127	115	118	113		
Diglycine nitrate at room temperature	127.2 (1.0)	114.1 (9)	118.6 (1.0)	112.1 (9)	0.162	<i>l</i>
	124.6 (9)	114.0 (8)	121.1 (9)	110.1 (8)	0.146	
at $-150^{\circ}\text{C}$	125.9 (1.2)	113.1 (1.1)	121.0 (1.2)	111.1 (1.1)	0.025	
	127.0 (1.2)	114.3 (1.1)	118.7 (1.2)	111.0 (1.0)	0.008	
Triglycine sulphate	125.9 (3.5)	115.1 (3.5)	115.3 (3.5)	109.3 (3.5)	0.000	<i>m</i>
	125.4 (3.5)	113.1 (3.5)	121.5 (3.5)	107.1 (3.5)	0.269	
	122.9 (3.5)	111.3 (3.5)	119.2 (3.5)	110.2 (3.5)	0.000	
	125.9	118.5§	115.3	108.7§	0.004§	
	125.4	113.1	121.5	107.1	0.269	
	126.4§	111.3	122.2§	111.5§	0.154§	
Copper glycine $\text{H}_2\text{O}$	123	118	119	115		<i>n</i>
	127	116	117	116		
	124.3 (1.0)	118.3 (1.0)	117.4 (1.0)	112.6 (1.0)	0.103	<i>o</i>
	122.8 (1.0)	119.7 (1.0)	117.5 (1.0)	111.3 (1.0)	0.162	
Nickel glycine $2\text{H}_2\text{O}$	122	123	115	103	0.27	<i>p</i>
	124.8 (9)	118.4 (7)	116.8 (7)	111.1 (6)	0.61	<i>q</i>
Platinum glycine	122.2 (5)	120.7 (5)	116.8 (4)	111.1 (5)	0.32	<i>r</i>
Diglycine barium chloride $\text{H}_2\text{O}$	124.2	116.0	119.8	111.7	0.158	<i>s</i>
Diglycine strontium chloride $3\text{H}_2\text{O}$	124.2	116.4	119.4	111.5	0.141	<i>s</i>
Diglycine manganous chloride	124.8	115.7	119.5	110.5	0.703	<i>s</i>
Cadmium glycine	121**	115**	123**	115**		<i>t</i>

\* The maximum deviation from the mean of the three sets of data at room temperature for GSN varies from 0.00 to 0.02 Å in the case of bond distances and  $1-2^{\circ}$  in the case of angles.

† Quoted in Iitaka (1961).

‡ Bond distances corrected for librations.

§ Calculated with the coordinates (in *Structure Reports*, 1959).

\*\* Calculated with the coordinates (by the authors).

Table 5 (cont.)

References: *a* This work; *b* Albrecht & Corey (1939); *c* Marsh (1958); *d* Iitaka (1959); *e* Iitaka (1960); *f* Iitaka (1958); *g* Iitaka (1961); *h* Hahn & Buerger (1957); *i* Hahn (1960); *j* Buerger, Barney & Hahn (1956); *k* Hahn (1959); *l* Sato (1968); *m* Hoshino, Okaya & Pepinsky (1959); *n* Tomita & Nitta (1961); *o* Freeman, Snow, Nitta & Tomita (1964); *p* Stosick (1945); *q* Freeman & Guss (1968); *r* Freeman & Golomb (1969); *s* Narayanan & Venkataraman (1970); *t* Low, Hirshfeld & Richards (1959).

The crystal structure of zinc glycine has been solved only in projection (Low, Hirshfeld & Richards, 1959). The details of the crystal structure analyses of glycine ferrous sulphate pentahydrate (Lindqvist & Rosenstein, 1960) and triglycine neodymium chloride trihydrate (Belyaeva, Porai-Koshits, Malinovskii, Aslanov, Sukhanova and Martynenko, 1969) are not known.

group symmetry  $2/m$ . In silver oxalate (Griffith, 1943; Ag-Ag=3.34 Å, Ag-O=2.17, 2.30 Å) and potassium silver carbonate [Barclay & Hoskins, 1963; Ag-Ag=3.00, 3.21 Å; Ag-O=2.09 (4) Å; O-Ag-O=170 (2)°] the molecules form infinite chains instead of dimers.

The sum of the covalent radii for silver and oxygen atoms is about 2.10 Å (Pauling, 1960). Ag<sub>2</sub>O represents a structure having this type of bond with a linear O-Ag-O coordination (Ag-O=2.04 Å; Ag-Ag=3.34 Å; Wyckoff, 1965). In KAgO, there are square groups of Ag<sub>4</sub>O<sub>4</sub> with the oxygens at the corners and the silvers at the centre of the edges of the square (Ag-O=2.17 Å; Ag-Ag=2.91 Å; O-Ag-O=174°; Sabrowsky & Hoppe, 1968). In crystals where the interaction between metal and oxygen is predominantly ionic, the expected Ag-O distance is about 2.5 Å (Helmholz & Levine, 1942). Structures representing this type are AgNO<sub>3</sub> (Lindley & Woodward, 1966), AgNO<sub>2</sub> (Long & Marsh, 1962), AgClO<sub>2</sub> (Cooper & Marsh, 1961) and AgClO<sub>3</sub> (Naray-Szabo & Pocza, 1942). It may, therefore, be concluded that the interactions Ag-O(1) ( $-x, -y, -z$ ) and Ag-O(2) in GSN are more covalent than ionic.

#### Dimensions of the glycine group

The dimensions of glycine in GSN, together with those found in other glycine structures are given in Table 5(a) and (b) as no such detailed comparison is available elsewhere. The atoms C(1), O(1), O(2) and C(2) (Figs. 3 and 4) are coplanar, the equations of the mean planes obtained from different sets of data being given in Table 6. The terminal nitrogen atom, N(1), is out of the mean plane by 0.33 Å and, as the non planarity of the glycine group normally indicates zwitterionic nature, the glycine group in GSN exists as NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>COO<sup>-</sup>. There is no significant difference between the two C-O bonds, and the C(1)-C(2) bond has the usual single bond length.

#### Dimensions of the nitrate group

The dimensions of the nitrate group are given in Table 7. The nitrate group is planar with the three N-O distances approximately equal within the accuracy of this work. The three O-N-O angles vary from 112 to 124° showing the absence of  $D_{3h}$  symmetry. The equa-

tion of the mean plane of the nitrate group for the four different sets of data is given in Table 8.

Table 6. Mean planes for the glycine group obtained from different sets of data (Blow, 1960)

The coefficients *A*, *B*, *C* and *D* are defined so that  $AX+BY+CZ+D=0$  where  $X=x+z\cos\beta$ ,  $Y=y$ ,  $Z=z\sin\beta$ . *A* represents the deviation of the atom in the parentheses from the mean plane. The nitrogen atom, N(1), was not included in the mean plane calculations.

	Set 1	Set 2	Set 3	Mean	Set 4 L.T.
<i>A</i>	-0.493	-0.541	-0.505	-0.513	-0.525
<i>B</i>	0.804	0.776	0.797	0.792	0.793
<i>C</i>	-0.333	-0.324	-0.332	-0.330	-0.309
<i>D</i>	0.274	0.384	0.301	0.320	0.340
$\Delta[C(1)]$	0.020 Å	-0.044 Å	0.011 Å	-0.004 Å	0.006 Å
$\Delta[C(2)]$	-0.006	0.012	-0.003	0.001	-0.002
$\Delta[O(1)]$	-0.007	0.016	-0.004	0.002	-0.002
$\Delta[O(2)]$	-0.007	0.017	-0.004	0.002	-0.002
$\Delta[N(1)]$	0.392	0.253	0.335	0.327	0.306

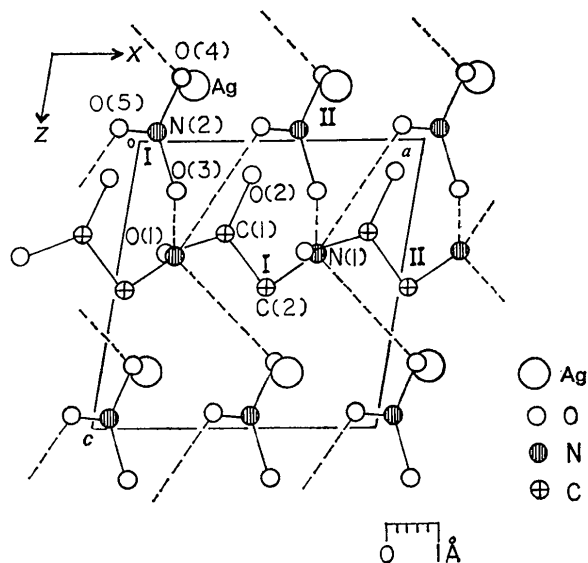


Fig. 6. A view of the hydrogen bonding (broken lines) in the structure. The atoms in asymmetric part I have the coordinates  $x, y, z$  and those in II have the coordinates  $\frac{1}{2}+x, \frac{1}{2}-y, z$ .

Table 7. *Dimensions of the nitrate group in the structure*

The maximum standard deviation as well as the maximum deviation from the mean value corresponding to the data sets 1, 2 and 3 at room temperature are given along with the values at low temperature.

	At room temperature			At low temperature	
	Mean value	Max. standard deviation	Max. deviation from the mean	Value	Standard deviation
<b>Distances (Å)</b>					
N(2)–O(3)	1.26	0.03	0.04	1.23	0.04
N(2)–O(4)	1.25	0.04	0.04	1.25	0.04
N(2)–O(5)	1.28	0.03	0.04	1.34	0.03
<b>Angles (°)</b>					
O(3)–N(2)–O(4)	123	2	2	124	3
O(3)–N(2)–O(5)	116	2	2	112	3
O(4)–N(2)–O(5)	120	2	2	124	3

Table 8. *Mean planes for the nitrate group obtained from different sets of data (Blow, 1960)*

The coefficients  $A$ ,  $B$ ,  $C$  and  $D$  are defined so that  $AX + BY + CZ + D = 0$  where  $X = x + z \cos \beta$ ,  $Y = y$ ,  $Z = z \sin \beta$ .  $\Delta$  represents the deviation of the atom in the parentheses from the mean plane.

	Set 1	Set 2	Set 3	Mean	Set 4 L.T.
$A$	-0.772	-0.769	-0.772	-0.771	-0.752
$B$	0.636	0.638	0.636	0.637	0.659
$C$	-0.010	-0.026	-0.017	-0.018	-0.020
$D$	-2.064	-2.103	-2.060	-2.076	-2.115
$\Delta$ [N(2)]	0.030 Å	0.072 Å	0.029 Å	0.044 Å	-0.006 Å
$\Delta$ [O(3)]	-0.010	-0.025	-0.009	-0.015	0.002
$\Delta$ [O(4)]	-0.011	-0.024	-0.010	-0.015	0.002
$\Delta$ [O(5)]	-0.009	-0.022	-0.009	-0.013	0.002

### Hydrogen bonding

Because of the zwitterionic nature of glycine as mentioned earlier, there are three protons attached to the terminal nitrogen atom N(1). There are three oxygen atoms (see Fig. 6) belonging to different nitrate groups at less than 3 Å from N(1), and directed towards the corners of a pyramid. These three bonds have, therefore, been identified as the N–H···O bonds in the structure. The relevant distances and the Donohue angles are presented in Table 9. The bond N(1)–H···O(3) ( $\frac{1}{2} + x, \frac{1}{2} - y, z$ ) is approximately perpendicular to the  $a$  axis and is almost parallel to the  $b$  axis, the polar direction in the ferroelectric phase.

### Packing

Figs. 2, 3 and 4 illustrate the packing of the molecules in the crystal structure. Dimers of glycines in neighbouring unit cells translated by  $c$  are connected by Ag–O(1) ( $x, y, z - 1$ ) resulting in infinite chains along the  $c$  axis. Apart from the hydrogen bonded N–H···O contacts mentioned above, there are three short contacts in the structure: C(1)–O(3), C(2)–O(3) and C(2)–O(5) ( $x + 1, y, z + 1$ ) (see Table 10). The dihedral angle between the glycine and the nitrate planes is 25°.

### Ferroelectricity and crystal structure

The only other glycine-containing ferroelectric crystals for which the structures have been solved are triglycine sulphate (TGS; Hoshino, Okaya & Pepinsky, 1959) and diglycine nitrate (DGN; Sato, 1968). Both these structures, in the paraelectric phase contain atoms or groups of atoms in special positions unlike the structure of GSN. In TGS, one of the three glycines lies on the mirror plane and the sulphur atom is at the intersection of the  $2_1$  screw and the mirror plane. In DGN, the nitrate group is disordered with the nitrogen occupying an inversion centre. In the ferroelectric phase, these atoms in both the crystals no longer occupy special positions. Also, in both these structures, there is a strong O–H···O bond (2.44 Å long) bridging two glycine oxygens, and the movement of the hydrogen atom along this bond is assumed to be responsible for the ferroelectric transitions.

From the infrared studies, Warriar & Narayanan (1967; see also Narayanan and Warriar, 1967) concluded that the rapid reorientation of the  $\text{NH}_3^+$  groups or alignment of the N–H···O bonds may not play any direct role in the ferroelectric behaviour of GSN. Easwaran (1966) from p.m.r. studies came to a similar conclusion that the protons do not play any part in the ferroelectric transition in the crystal. These authors suggested that silver played an important role. As mentioned in the introduction, the partial substitution of silver by lithium or thallium in GSN elevates its Curie point. The silver atom and its position in the structure are therefore likely to have the most prominent role in the phase transition of this crystal. As described earlier, the silver atoms occupy the centres of O–Ag–O bonds between centrosymmetrically related glycines, the entire group of atoms (except for the end nitrogens and the hydrogens) having the  $2/m$  symmetry. On the lowering of temperature, the silver atoms are likely to move in such a way that this inversion centre is lost, giving rise to ferroelectricity in the crystal.

The authors thank Professor P. S. Narayanan for many valuable discussions and Professor R. S. Krishnan for his interest in this work. They thank the Neutron Diffraction Group of the Bhabha Atomic Research Centre, Bombay and the Crystallography Group of the University of Madras for permission to use some of their programs. One of the authors (J.K. M.R.) thanks the Council of Scientific and Industrial Research, New Delhi, for the award of a Senior Research Fellowship.

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Table 9. *Hydrogen bond distances and Donohue angles*

The maximum standard deviation as well as the maximum deviation from the mean value corresponding to the data sets 1, 2 and 3 at room temperature are given along with the values at low temperature.

	At room temperature			At low temperature	
	Mean value	Max. standard deviation	Max. deviation from the mean	Value	Standard deviation
<b>Distances (Å)</b>					
N(1)-O(3) ( $\frac{1}{2} + x, \frac{1}{2} - y, z$ )	2.88	0.03	0.02	2.89	0.04
N(1)-O(5) ( $x + 1, y, z$ )	2.93	0.04	0.04	2.81	0.04
N(1)-O(4) ( $x + 1, y, z + 1$ )	2.97	0.03	0.02	2.93	0.04
<b>Angles (°)</b>					
O(3) ( $\frac{1}{2} + x, \frac{1}{2} - y, z$ ) - N(1) - C(2)	133	2	2	135	2
O(5) ( $x + 1, y, z$ ) - N(1) - C(2)	132	2	0	133	2
O(4) ( $x + 1, y, z + 1$ ) - N(1) - C(2)	110	2	2	110	2
O(3) ( $\frac{1}{2} + x, \frac{1}{2} - y, z$ ) - N(1) - O(5) ( $x + 1, y, z$ )	78	1	0	76	1
O(3) ( $\frac{1}{2} + x, \frac{1}{2} - y, z$ ) - N(1) - O(4) ( $x + 1, y, z + 1$ )	88	1	1	88	1
O(4) ( $x + 1, y, z + 1$ ) - N(1) - O(5) ( $x + 1, y, z$ )	106	1	1	105	1

Table 10. *Short contacts in the structure*

The maximum standard deviation as well as the maximum deviation from the mean value corresponding to the data sets 1, 2 and 3 at room temperature are given along with the values at low temperature.

	At room temperature			At low temperature	
	Mean value	Max. standard deviation	Max. deviation from the mean	Value	Standard deviation
<b>Distances (Å)</b>					
C(1)-O(3)	2.95	0.03	0.07	2.98	0.04
C(2)-O(5) ( $x + 1, y, z + 1$ )	2.95	0.04	0.05	2.96	0.03
C(2)-O(3)	3.06	0.03	0.02	3.11	0.04
<b>Angle (°)</b>					
C(2)-C(1)-O(3)	79	1	3	80	1

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*Acta Cryst.* (1972). **B28**, 1496

## The Determination of Absolute Configuration and $\Delta f''$ Values for Light-Atom Structures\*

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(Received 10 August 1971)

The absolute configurations of 7 compounds containing only C, H and O atoms have been determined by careful measurement of about 20 Bijvoet differences for each compound using Cu  $K\alpha$  radiation. A highly significant indication was obtained even in unfavourable cases with poorly refined structures ( $R > 10\%$ ) or structures with very low oxygen content. A comparison of  $R$  values for the two enantiomers without considering the Bijvoet differences did not give significant indications. The generally weak intensities were measured with high precision using an alternating procedure and were corrected for absorption. Multiple diffraction was identified as an important cause of systematic errors. A value of  $0.0182 \pm 0.0008$  for the quantity  $\Delta f_{O:C}$  was deduced from the measurements. Values of  $n = 2.78 \pm 0.06$  and  $C = 4.66 \pm 0.25$  were calculated for the parameters in the empirical relation

$$\Delta f'' = C(\lambda/\lambda_K)^{n-1}$$

using the above result and Zachariasen's data on quartz.  $\Delta f''$  values obtained from the above equation agree well with Cromer's values calculated from atomic wave functions assuming  $n = 2.75$  for the  $K$  shells. The importance of obtaining further experimental values of  $\Delta f''$  is stressed.

### Introduction

The determination of absolute configuration by X-ray methods has recently been extended to light-atom structures using the very small anomalous scattering power of oxygen (Hope & de la Camp, 1969; Thiessen

& Hope, 1970; Moncrief & Sims, 1969; Neidle & Rogers, 1970). The methods used were the 'Bijvoet method' (measurement of Bijvoet differences) and the ' $R$  method' (see Hamilton, 1965, example 4) modified by limiting the  $R$ -value comparison of the two enantiomers to a set of 'sensitive' reflexions.

In this paper the techniques of measurement and statistical evaluation developed during the course of an investigation of 7 substances are reported. The refined method is now capable of producing significant results in unfavourable (practical) cases. The power of

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