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Structure of diaquabisglycinemagnesium(II) bromide

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Abstract : The crystal structure of diaquabisglycinemagnesium(II) bromide has been determined from the intensity data collected using a CAD-4 diffractometer with MoK α radiation. The crystals are monoclinic with a = 8.819(3) Å, b = 6.089(1) Å, c = 11.823(3) Å, β = 111.88(3)°, Z = 2 and belongs to the space group $P2_1/a$. The structure was determined by Patterson and Fourier methods. Least-squares refinements led to R = 0.037 and R_w = 0.039. Magnesium is coordinated to six oxygen atoms, four from the carboxyl group of the two centrosymmetrically related glycine molecules and the rest from the water molecules, forming an octahedron with minimal distortions. The bromine atoms do not coordinate with magnesium, but fill in the vacant spaces and participate in hydrogen bonding. The glycine molecules exist as zwitterions, $NH_3^+CH_2COO^-$.

Keywords : Glycine, amino acid adduct, crystal structure

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1. Introduction

In view of the chemical and biological importance of the amino acids, a systematic investigation of several complexes of amino acids with inorganic salts is being carried out in our laboratory. Magnesium is one of the elements essential for life since it is found constantly in small amount in blood, being distributed about equally between cells and plasma. The structure of a complex of glycine and $MgBr_2$ is presented here. This structure is probably the first case of a complex of amino acid with a magnesium salt.

2. Experimental

Transparent, colourless single crystals of $Mg(NH_3^+CH_2COO^-)_2Br_2.2H_2O$ were obtained from a saturated aqueous solution containing glycine and $MgBr_2$ in stoichiometric ratio, in 2 : 1 proportion. The crystal belongs to the space group $P2_1/a$ with a = 8.819(3) Å, b = 6.089(1) Å, c = 11.823(3) Å, β = 111.88(3)°, V = 589.2(3) Å^3, F.W. = 371.97,

d_{expt} = 1.89 g cm^{-3}, d_{calc} = 1.86 g cm^{-3} and Z = 2. The density was determined by floatation method using a liquid-mixture of bromoform and carbon tetrachloride.

The three-dimensional intensity data were collected using a CAD-4 diffractometer, with graphite monochromated MoKα radiation, at the RSIC, Indian Institute of Technology, Madras. The data were collected at room temperature (18 ± 1°C) using the ω–2θ scan technique to a maximum 2θ value of 50.0°. Of the 1219 reflections which were collected, 1010 were unique. The intensities of the two representative reflections [(2 2 0) and (–3 2 3)] which were measured after every 230 reflections remained constant throughout the data collection indicating the crystal and electronic stability. Hence, no decay correction was applied. The data were corrected for absorption, Lorentz and polarization effects.

3. Determination and refinement of the structure

A three-dimensional Patterson synthesis revealed the positions of the bromine and magnesium atoms. Then, a difference Fourier synthesis was carried out. From this, the positions of all the non-hydrogen atoms were determined and two cycles of least-squares refinement with isotropic temperature factors for the non-hydrogen atoms led to an R value of 0.11. Then,

Table 1. The fractional coordinates (× 10^4) of the atoms in the unit cell. The e.s.d.'s are given in parentheses

Atom	x	y	z
Mg	0000	5000	0000
Br	1511 (0)	1975 (1)	3905 (0)
OW	3843 (3)	–2630 (4)	8949 (2)
O1	2794 (3)	1706 (4)	9476 (2)
O2	4444 (3)	–1278 (4)	11428 (2)
N	0400 (4)	2890 (5)	6314 (3)
C1	1726 (4)	2527 (5)	8569 (3)
C2	1839 (4)	2129 (6)	7335 (3)
H1OW	3641	–2745	8133
H2OW	3017	–3207	9192
H1N	0045	4170	6523
H2N	0532	2978	5588
H3N	–0353	1910	6146
H1C2	2125	0698	7244
H2C2	2953	2931	7395

*Hydrogen atoms were not included in the refinement. Their isotropic temperature factors were fixed at 0.05 Å.

anisotropic temperature factors were introduced for all the non-hydrogen atoms and after two cycles of least-squares refinement the R value was found to be 0.05. All the hydrogen atoms were located from a difference map. They were not included in the refinement. Their isotropic

temperature factors were fixed at 0.05 $Å^2$. The maximum value of shift/esd was 0.004 in the final cycle. The final value of $R = 0.037$ and $R_W = 0.039$. The weighting scheme employed

Table 2. Anisotropic thermal parameters ($\times 10^4$) of the non-hydrogen atoms The e s.d 's are given in parentheses

Atom	U11	U22	U33	U12	U13	U23
Mg	141 (6)	187 (7)	131 (7)	−5 (6)	50 (6)	4 (5)
Br	435 (3)	256 (3)	238 (3)	6 (1)	166 (2)	6 (1)
OW	440 (16)	345 (13)	245 (16)	−170 (13)	180 (14)	−81 (13)
O1	202 (11)	368 (13)	185 (13)	110 (9)	72 (10)	58 (10)
O2	190 (10)	271 (12)	161 (11)	−71 (19)	74 (9)	17 (10)
N	312 (16)	283 (17)	191 (15)	33 (11)	103 (14)	10 (10)
C1	169 (15)	148 (13)	233 (18)	−45 (12)	100 (14)	−40 (14)
C2	240 (17)	311 (20)	204 (19)	142 (13)	98 (15)	36 (13)

in the final cycle had the form $w = 0.9451/[\sigma^2(F) + 0.00275\ F^2]$. The crystallographic programs used were SHELX 76 [1] and SHELX 400 [2]. All the computations were carried out using the CYBER 180/830 A system at the Department of Computer Science of our University The final atomic positions are given in Table 1 and the anisotropic thermal

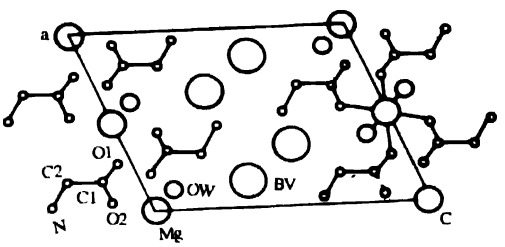

Figure 1. Projection of the crystal structure down the *b*-axis

parameters in Table 2. A list of observed and calculated structure factors may be obtained from the authors on request. The projection of the crystal structure down the *b*-axis is shown in Figure 1.

4. Description and discussion

In this crystal structure, the glycine molecules are found to be coordinated to the metal atom by bidental bridging. The magnesium atom is coordinated to six oxygen atoms, four from each of the centrosymmetrically related glycine molecules and two from the water molecules, forming an octahedron with minimal distortions. The dimensions of the octahedral coordination around magnesium is given in Table 3. The octahedral surrounding for the magnesium is also shown in Figure 1.

The geometry of the glycine molecule is normal as found in other similar structures [3–5]. The glycine molecules exist in this crystal as zwitterions, $NH_3^+CH_2COO^-$. This is

evident from the facts that the C–O distances and the bond angles around the carbon atom of the carboxylic group have values expected for such configuration and also three hydrogen

Table 3. Dimensions of the Mg–O octahedra in the structure

Mg - OW	=	2 051 (3) Å
Mg – OW'	=	2 051 (3) Å
Mg - O2	=	2.077 (3) Å
Mg - O2'	=	2 077 (3) Å
Mg - O1	=	2 086 (3) Å
Mg - O1'	=	2 086 (3) Å
OW - Mg - OW'	=	180 0 (1)°
OW – Mg – O2'	=	90 8 (1)°
OW Mg – O2	=	89 2 (1)°
OW – Mg – O1	=	90 5 (1)°
OW Mg – O1'	=	89 5 (1)°
OW' – Mg – O2'	=	89 2 (1)°
OW' - Mg – O2	=	90 8 (1)°
OW' – Mg O1	=	89 5 (1)°
OW' Mg – O1'	=	90 5 (1)°
O2' Mg - O2	=	180 0 (1)°
O2' – Mg O1	=	92 8 (1)°
O2' – Mg O1'	=	87 2 (1)°
O2 - Mg O1	=	87 2 (1)°
O2 – Mg – O1'	=	92 8 (1)°
O1 – Mg – O1'	=	180.0 (1)°

atoms are located around the nitrogen atom. The bond lengths and bond angles of the glycine molecule are listed in Table 4. The torsion angles O1–C1–C2–N1 and O2–C1–C2–N1 have the values 171.6° and –156.5°, respectively.

Table 4. Bond lengths (Å) and bond lengths (°) of the glycine molecule in the structure

C1–O1 = 1 243 (4)	O1–C1–O2 = 126 1 (4)
C1 O2 = 1 256 (5)	O1–C1–C2 = 116.8 (4)
C1–C2 = 1 515 (7)	O2–C1–C2 = 117 1 (4)
C2 N1 = 1 477 (5)	C1–C2–N1 = 112.6 (4)
H1N N = 0 819	H1N N–H2N = 113 9 (4)
H2N–N = 0 897	H1N–N–H3N = 105.4 (4)
H3N–N = 0 964	H2N–N–H3N = 98 9 (3)
H1C2–C2 = 0 936	H1C2–C2–H2C2 = 111 9 (4)
H2C2–C2 = 1.055	
	H1OW–OW–H2OW = 102.8 (4)
H1OW–OW = 0 814	
H2OW–OW = 1 008	

The halogens do not participate in metal coordination and are involved only in hydrogen bonding. The amino group forms three N–H...Br hydrogen bonds. The water oxygen forms one OW–H...Br and one OW–H...O (the oxygen belonging to the carboxyl group) hydrogen bonds.

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