

Structure of Tris(glycine)calcium(II) Dibromide

BY J. K. MOHANA RAO AND S. NATARAJAN

School of Physics, Madurai Kamaraj University, Madurai-625 021, India

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Abstract

Tris(glycine)calcium(II) dibromide, $[\text{Ca}(\text{C}_2\text{H}_5\text{NO}_2)_3]\cdot\text{Br}_2$, $\text{C}_6\text{H}_{15}\text{CaN}_3\text{O}_6^{2+}\cdot 2\text{Br}^-$, crystallizes in an orthorhombic unit cell of dimensions $a = 9.15$ (1), $b = 14.84$ (2) and $c = 20.31$ (2) Å, in the space group $Pbc2_1$, with $Z = 8$. This non-centrosymmetric crystal structure, having 36 non-hydrogen atoms in the asymmetric unit, of which six are Ca and Br atoms, has been determined using a three-dimensional Patterson synthesis, a minimum function and a Fourier synthesis, with 1612 visually estimated photographically registered reflections. With anisotropic thermal parameters for the Ca and Br atoms and isotropic for the other non-hydrogen atoms, the final R was 0.095. Each of the two Ca atoms is coordinated to six O atoms and a Br atom. The two Ca coordination polyhedra in the structure are linked to form distorted pentagonal bipyramids. A hydrogen-bonding scheme has been proposed based on the interatomic distances in the structure.

Introduction

The crystal structures of many addition compounds of glycine with inorganic acids and metallic salts and also many metal complexes of glycine are known (Natarajan, 1979). However, no structural data on any Ca complex of glycine are available. The only work reported in this field was the preliminary X-ray crystallographic data for the calcium chloride complex of glycine (Jayalakshmi & Vijayan, 1967), until the present authors started investigations of such compounds in their laboratory. Because of the biological and chemical importance of both glycine and calcium, a series of glycine complexes with calcium halides, *viz* CaCl_2 , CaBr_2 and CaI_2 , were crystallized and their structures studied (Natarajan & Mohana Rao, 1976*a,b*, 1977; Natarajan, 1979). In this paper, the crystal structure of the title compound is reported.

Experimental

Single crystals of the complex (hereafter GCB) were grown at room temperature by slow evaporation of a

saturated aqueous solution containing glycine and calcium bromide. From the preliminary Weissenberg photographs the space group was found to be either $Pbcm$ or $Pbc2_1$. Three-dimensional X-ray diffraction data were collected by equi-inclination Weissenberg photographic techniques, using $\text{Cu } K\alpha$ radiation. Intensities of 1612 independent reflections were estimated visually and the necessary corrections were applied.

Structure determination and refinement

The absence of any $(0,0,w)$ peak in the three-dimensional Patterson function showed that the space group could only be the non-centrosymmetric $Pbc2_1$ (with equivalent positions x,y,z ; $-x, -y, \frac{1}{2} + z$; $-x, \frac{1}{2} + y, z$; $x, \frac{1}{2} - y, \frac{1}{2} + z$) and, therefore, the alternative centrosymmetric space group $Pbcm$ was eliminated. Using the Patterson function and also a minimum function (both in three dimensions) drawn with respect to a Ca–Ca Patterson peak, the positions of the four Br atoms were determined. Based on the positions of the four Br atoms and one Ca atom, two cycles of structure factor least-squares calculations were carried out, which yielded an R factor ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.317. From successive Fourier and difference syntheses and model building, all the non-hydrogen atoms were located. For all cycles of refinement, the full-matrix structure factor least-squares refinement program *LALS* (originally written by P. K. Gantzel, R. A. Sparks & K. N. Trueblood and modified later by Dr Liminga of Uppsala and also at the University of Madras) was used. The function minimized was $\sum w(|F_o| - k|F_c|)^2$, where k is the scale factor and the weights are as suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961): $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$, with $a = 11.5$, $c = 0.004$ and $d = 0.00002$. The atomic scattering factors used were those of Cromer & Waber (1965) for Ca^{2+} , Br^- and neutral C, N and O atoms. Dispersion corrections (Cromer & Liberman, 1970) were applied for the Ca and Br atoms. The Ca and Br atoms were treated anisotropically and all other atoms were refined with isotropic temperature factors. The z coordinate of Br(1) was used to fix the

Table 1. Fractional atomic coordinates and their temperature factors, with *e.s.d.*'s in parentheses

For Br and Ca, the *B* values listed in this table are the equivalent isotropic temperature factors.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Br(1)	-0.2581 (5)	0.1786 (3)	0.3544	4.2 (1)
Br(2)	0.2715 (5)	0.2044 (2)	0.3754 (3)	4.0 (1)
Br(3)	0.2297 (5)	0.4205 (3)	0.2450 (2)	4.2 (1)
Br(4)	-0.2455 (5)	0.4623 (2)	0.2391 (2)	3.4 (1)
Ca(1)	0.1757 (7)	0.2378 (3)	0.0059 (4)	2.3 (1)
Ca(2)	0.3261 (7)	0.0138 (3)	0.0999 (4)	2.3 (1)
O(11)	0.172 (3)	0.142 (1)	0.120 (1)	2.6 (4)
O(21)	0.037 (3)	0.262 (2)	0.111 (1)	3.3 (4)
C(11)	0.083 (4)	0.197 (2)	0.145 (2)	2.8 (6)
C(21)	0.050 (4)	0.178 (2)	0.218 (2)	3.0 (6)
N(11)	-0.032 (3)	0.260 (2)	0.239 (2)	3.6 (5)
O(12)	0.326 (3)	0.112 (1)	-0.005 (1)	3.6 (4)
O(22)	0.467 (3)	-0.010 (2)	-0.001 (1)	3.1 (4)
C(12)	0.407 (4)	0.055 (2)	-0.032 (1)	2.2 (5)
C(22)	0.459 (5)	0.073 (2)	-0.103 (2)	3.5 (7)
N(12)	0.531 (4)	-0.009 (3)	-0.131 (2)	5.3 (8)
O(13)	0.068 (2)	0.381 (1)	0.003 (1)	2.9 (4)
O(23)	-0.131 (3)	0.443 (2)	0.049 (1)	3.3 (4)
C(13)	0.004 (3)	0.433 (2)	0.042 (1)	1.3 (4)
C(23)	0.097 (4)	0.492 (2)	0.088 (2)	2.8 (5)
N(13)	0.258 (3)	0.485 (2)	0.076 (1)	3.2 (5)
O(14)	0.371 (3)	0.307 (1)	0.061 (1)	2.8 (4)
O(24)	0.570 (2)	0.370 (1)	0.106 (1)	2.4 (3)
C(14)	0.506 (4)	0.321 (2)	0.065 (2)	3.5 (8)
C(24)	0.590 (4)	0.258 (2)	0.018 (2)	2.7 (5)
N(14)	0.750 (3)	0.266 (2)	0.032 (1)	2.6 (4)
O(15)	-0.207 (3)	0.063 (1)	-0.058 (1)	3.3 (4)
O(25)	-0.041 (3)	0.165 (1)	-0.029 (1)	2.9 (4)
C(15)	-0.083 (3)	0.096 (2)	-0.059 (1)	2.4 (5)
C(25)	0.037 (5)	0.054 (3)	-0.103 (2)	4.3 (8)
N(15)	-0.019 (3)	-0.029 (2)	-0.136 (1)	3.0 (5)
O(16)	0.707 (3)	0.187 (2)	0.169 (1)	4.2 (5)
O(26)	0.529 (3)	0.097 (1)	0.132 (1)	2.9 (4)
C(16)	0.580 (4)	0.157 (2)	0.169 (1)	2.5 (5)
C(26)	0.467 (4)	0.210 (2)	0.210 (1)	2.3 (5)
N(16)	0.528 (4)	0.291 (2)	0.244 (2)	4.8 (7)

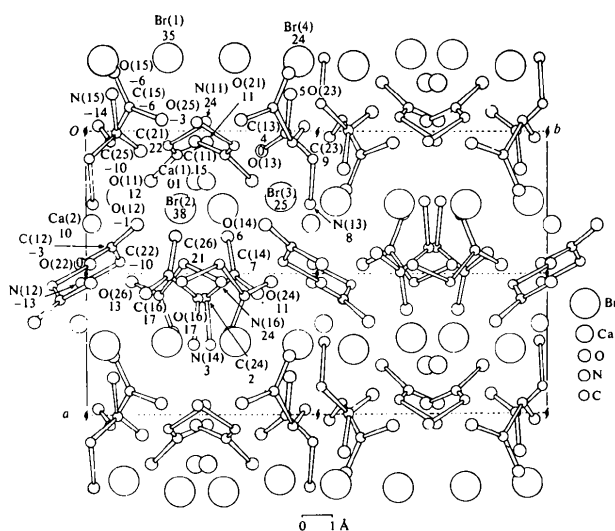


Fig. 1. The crystal structure of GCB viewed down the *c* axis. The heights ($\times 100$) of the atoms in the asymmetric part are also given next to the atom labels.

origin and this parameter was not refined. Refinement was terminated when the shifts were considerably less than the standard deviations. The final *R* for 1583 reflections was 0.095, after removal of 29 reflections which were suspected of being in error. Including all 1612 reflections, *R* was 0.108. The final positional parameters and temperature factors are listed in Table 1.* A view of the crystal structure is shown in Fig. 1. It is interesting to note the presence of a non-crystallographic inversion centre at (280, 42, 20)/360 and its equivalent positions.

Discussion

Coordination of calcium

There are two Ca atoms in the asymmetric part of the unit cell and each has seven nearest neighbours, the coordination polyhedra being pentagonal bipyramids (Fig. 2). Table 2 lists the relevant distances and angles in the two coordination polyhedra. The two pentagonal bipyramids share the edge connecting O(11) and O(12) and extend in infinite chains linked by four glycine molecules. In the three crystal structures of the

* Lists of structure factors, phase angles, anisotropic thermal parameters for the heavy atoms and hydrogen-bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34991 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

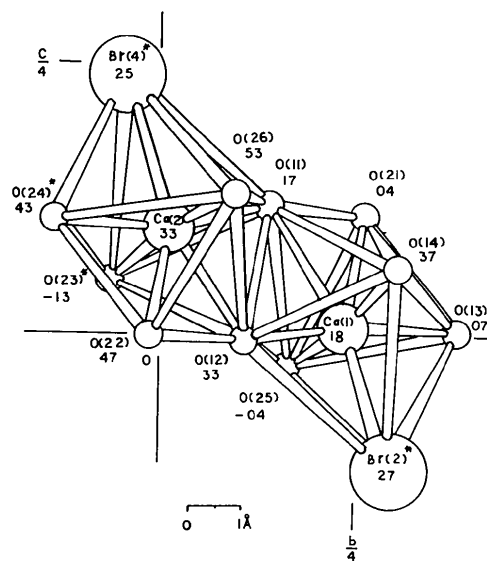


Fig. 2. A view of the two pentagonal bipyramids occurring in the crystal structure of GCB. The heights ($\times 100$) of the atoms are also given below the atoms. O(23)*, O(24)*, Br(2)* and Br(4)* represent those atoms at the respective positions II, III, I and II of the symmetry codes as given in Table 2.

Table 2. *Dimensions of the calcium-oxygen polyhedra in GCB with e.s.d.'s in parentheses*

Bond distances are in Å and bond angles in degrees.

Polyhedron (1)		Polyhedron (2)	
Ca(1)—O(13)	2.34 (2)	Ca(2)—O(23) ^{II}	2.32 (3)
Ca(1)—O(12)	2.34 (2)	Ca(2)—O(26)	2.33 (2)
Ca(1)—O(14)	2.35 (2)	Ca(2)—O(24) ^{III}	2.34 (2)
Ca(1)—O(25)	2.37 (3)	Ca(2)—O(11)	2.41 (2)
Ca(1)—O(21)	2.51 (2)	Ca(2)—O(22)	2.45 (3)
Ca(1)—O(11)	2.72 (2)	Ca(2)—O(12)	2.57 (2)
Ca(1)—Br(2) ^I	2.92 (1)	Ca(2)—Br(4) ^{II}	3.02 (1)
O(14)—Ca(1)—O(25)	168.9 (8)	O(23) ^{II} —Ca(2)—O(26)	169.4 (9)
O(14)—Ca(1)—O(21)	85.3 (8)	O(23) ^{II} —Ca(2)—O(24) ^{III}	85.4 (8)
O(14)—Ca(1)—O(11)	80.3 (7)	O(23) ^{II} —Ca(2)—O(11)	89.3 (8)
O(14)—Ca(1)—Br(2) ^I	94.3 (6)	O(23) ^{II} —Ca(2)—O(22)	87.9 (8)
O(14)—Ca(1)—O(12)	86.8 (8)	O(23) ^{II} —Ca(2)—O(12)	83.5 (8)
O(14)—Ca(1)—O(13)	86.3 (8)	O(23) ^{II} —Ca(2)—Br(4) ^{II}	96.7 (6)
O(25)—Ca(1)—O(21)	84.1 (8)	O(26)—Ca(2)—O(24) ^{III}	98.3 (8)
O(25)—Ca(1)—O(11)	90.4 (7)	O(26)—Ca(2)—O(11)	90.0 (8)
O(25)—Ca(1)—Br(2) ^I	96.5 (6)	O(26)—Ca(2)—O(22)	83.8 (8)
O(25)—Ca(1)—O(12)	95.8 (8)	O(26)—Ca(2)—O(12)	86.1 (8)
O(25)—Ca(1)—O(13)	93.0 (8)	O(26)—Ca(2)—Br(4) ^{II}	93.8 (6)
O(13)—Ca(1)—O(21)	71.3 (8)	Br(4) ^{II} —Ca(2)—O(11)	84.1 (5)
O(21)—Ca(1)—O(11)	48.8 (7)	O(11)—Ca(2)—O(12)	72.2 (7)
O(11)—Ca(1)—O(12)	70.6 (7)	O(12)—Ca(2)—O(22)	52.4 (8)
O(12)—Ca(1)—Br(2) ^I	88.6 (6)	O(22)—Ca(2)—O(24) ^{II}	72.3 (8)
Br(2) ^I —Ca(1)—O(13)	80.8 (6)	O(24) ^{III} —Ca(2)—Br(4) ^{II}	79.7 (5)

Symmetry code: (I) $x, \frac{1}{2} - y, \frac{1}{2} + z - 1$; (II) $-x, \frac{1}{2} + y - 1, z$; (III) $-x + 1, \frac{1}{2} + y - 1, z$.

complexes of glycine with calcium halides, only in this, the calcium bromide complex, does the halogen atom coordinate with the calcium. The other rare examples in which the halogen takes part in coordination with Ca are the crystal structures of calcium bromoborate (Lloyd, Levasseur & Fouassier, 1973), calcium bromide-tetramethanol and calcium bromide-tetraethanol (Bois, Philoche-Levisalles & L'Haridon, 1978), and a few others. Probably the lack of further available O atoms, which seem to be preferred by calcium for coordination, is the reason for the coordination of the Br to Ca.

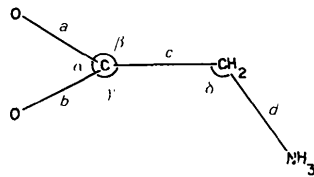
The volumes of the pentagonal bipyramids, determined using a method of calculation developed by Natarajan, Vijayakumar & Mohana Rao (1980), are 30.0 and 32.8 Å³. The pentagonal-bipyramidal coordination for Ca is found in a large number of crystal structures and some typical examples are those of tris(glycine)calcium(II) diiodide.H₂O (Natarajan, 1979; Natarajan & Mohana Rao, 1977) and calcium barbital.3H₂O (Berking, 1972).

Of the six O atoms of the glycine molecules which are involved in the Ca coordination, two [O(11) and O(12)] are shared by the two adjacent pentagonal bipyramids and, therefore, effectively only one O atom is coordinated per Ca. The other four O atoms are coordinated to only one Ca atom. Therefore, in total five O atoms, all contributed by the glycine molecules, are required for the coordination of each Ca atom in this crystal structure. This will require a minimum of

three glycine molecules per Ca. This is probably why the complex crystallizes with the formula (NH₂CH₂-COOH)₃.CaBr₂. If a sufficient number of waters of crystallization were available, the water O atoms would be used for Ca coordination instead of the Br atoms and probably three glycine molecules might not be necessary and the complex would probably have the formula (NH₂CH₂COOH)₂.CaBr₂.xH₂O. In fact, such a complex with $x = 4$ has been reported (Richter, 1942) whose structure has yet to be determined.

Glycine molecules

There are six non-equivalent glycine molecules in this crystal structure and their dimensions are listed in Table 3. All six glycine molecules are believed to exist in the crystal as zwitterions, NH₃⁺CH₂COO⁻, since the two C—O distances in each glycine molecule are approximately the same and there are three hydrogen bonds around each N atom. Also, this complex is just an addition compound of glycine with the inorganic salt CaBr₂. The O—O—C—C^α groups are planar and the terminal N atoms deviate from the mean planes by 0.25, 0.34, 0.11, 0.17, 0.04 and 0.16 Å, all with e.s.d.'s of 0.04 Å, and the dihedral angles (the angle between the O—O—C—C^α and the C—C^α—N planes) are 9.2, 16.0, 5.3, 6.0, 2.2 and 5.6°, all with e.s.d.'s of 1.0°. Both O atoms in two of the six glycine molecules are involved in coordination, resulting in bidentate chelation with Ca. The other glycine molecules are involved in unidentate coordination. In all, bidentate chelation as well as bridging and unidentate coordination occur in this crystal structure; numerous examples of similar structures exist (Natarajan, 1979).

Table 3. *Bond lengths (Å) and bond angles (°) for the glycine molecules in GCB, with e.s.d.'s in parentheses*


	Glycine molecule					
	1	2	3	4	5	6
Bond length						
a	1.25 (4)	1.25 (4)	1.25 (4)	1.25 (4)	1.25 (4)	1.25 (4)
b	1.25 (4)	1.27 (4)	1.25 (3)	1.25 (4)	1.24 (4)	1.25 (4)
c	1.54 (5)	1.54 (5)	1.54 (4)	1.54 (5)	1.54 (5)	1.54 (4)
d	1.50 (5)	1.50 (5)	1.50 (5)	1.50 (4)	1.50 (5)	1.50 (5)
Bond angle						
α	120 (3)	124 (3)	127 (3)	127 (3)	127 (3)	127 (3)
β	113 (3)	118 (3)	114 (2)	111 (3)	113 (3)	116 (3)
γ	127 (3)	117 (3)	119 (2)	122 (3)	120 (3)	116 (3)
δ	103 (3)	110 (3)	114 (2)	109 (3)	111 (3)	114 (3)

Hydrogen bonding

Since all six glycine molecules exist as zwitterions, 18 hydrogen bonds involving the terminal N atoms are expected. A hydrogen-bonding scheme* has been proposed based on the interatomic distances in this crystal structure. A tetrahedral environment for the N atom is assumed in the proposal of these hydrogen bonds. In some cases, the model has shown that the H atoms of the NH_3^+ group can exist between two acceptors. In such cases, it is possible that bifurcated hydrogen bonds are present.

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* See deposition footnote.

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The Structure of Dicarboxyl(η^4 -cinnamaldehyde)(triphenylphosphine)iron(0)

BY M. SACERDOTI, V. BERTOLASI AND G. GILLI

Centro di Strutturistica Diffraattometrica, Università di Ferrara, Ferrara, Italy

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Abstract

$\text{C}_{29}\text{H}_{23}\text{FeO}_3\text{P}$, $M_r = 506.3$, monoclinic, $P2_1/c$, $a = 9.729$ (3), $b = 9.277$ (3), $c = 27.523$ (5) Å, $\beta = 105.40$ (2)°, $Z = 4$, $D_c = 1.40$ Mg m $^{-3}$, $\mu(\text{Mo K}\alpha) = 0.669$ mm $^{-1}$. The crystal structure has been determined and refined from diffractometer data to an R of 0.036. The compound is a π complex and can be written as $[\text{Fe}(\text{CO})_2(\eta^4\text{-PhCH}=\text{CHCH}=\text{O})\text{PPh}_3]$. It displays a nearly square-pyramidal coordination with the PPh_3 group in an apical position and the two outer atoms of the heterodiene group and the two carbonyl groups in basal positions. The differences in bond distances between $[\text{Fe}(\text{CO})_2(\eta^4\text{-PhCH}=\text{CHCH}=\text{O})\text{PPh}_3]$ and $[\text{Fe}(\text{CO})_3(\eta^4\text{-PhCH}=\text{CHCH}=\text{O})]$ are interpreted in terms of the different π acidities of PPh_3 and CO.

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Crystals of $[\text{Fe}(\text{CO})_2(\eta^4\text{-PhCH}=\text{CHCH}=\text{O})\text{PPh}_3]$ were prepared by reacting triphenylphosphine and $[\text{Fe}(\text{CO})_3(\eta^4\text{-PhCH}=\text{CHCH}=\text{O})]$ in de-aerated benzene as part of a wider study on the mechanism and equilibrium constants of the reaction between (η^4 -heterodiene)iron tricarbonyl complexes and Group V ligands such as PPh_3 and AsPh_3 (Cardaci & Bellachioma, 1977). The molecular structure of the title compound was tentatively established by comparing its IR and NMR spectra with those of other compounds of known molecular structure, namely $[\text{Fe}(\text{CO})_3(\eta^4\text{-CH}_2=\text{CHCH}=\text{CH}_2)]$ (Mills & Robinson, 1963; Davis & Speed, 1970) and $[\text{Fe}(\text{CO})_3(\eta^4\text{-PhCH}=\text{CHCH}=\text{O})]$ (De Cian & Weiss, 1972a). Both compounds were shown to have a square-pyramidal structure with the diene ligand and the two CO groups occupying the four basal positions and with the other CO group in the apical position, and by comparison of their spectral