Synthesis and structural characterization of a calcium coordination polymer based on a μ₃-bridging tetradentate binding mode of glycine[#]

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Abstract. A new coordination polymer namely $[[Ca_6(H–gly)_{12}(H_2O)_{18}]Cl_{12}\cdot 6H_2O]_n$ (**1**) (H–gly = glycine) has been isolated from the calcium chloride–glycine–water system and structurally characterized. Each Ca(II) in **1** is eight-coordinated and is bonded to eight oxygen atoms three of which are from terminal water molecules and five oxygen atoms from four symmetry related zwitterionic glycine ligands. The H–gly ligands exhibit two different binding modes viz. a monodentate carboxylate ligation and a μ₃-tetradentate bridging carboxylate binding mode, which results in the formation of a one-dimensional coordination polymer. In the infinite chain the Ca(II) atoms are organized in a zigzag fashion. A comparative study reveals a rich and diverse structural chemistry of calcium halide–glycine compounds.

Keywords. Coordination polymer; calcium; glycine; zwitter ion; eight coordination.

1. Introduction

Variable structural chemistry, affinity for O-donor ligands, relevance in biology, non-toxic nature, aqueous solubility of many *s*-block compounds, are some factors responsible for the current interest in the chemistry of the closed shell *s*-block elements. Recent developments in the chemistry of *s*-block coordination compounds have been reviewed by Fromm.[1] Of the *s*-block elements, the structural chemistry of calcium has been well investigated. Many research groups have analysed the structural data in the Cambridge Structural Database (CSD) and Protein Data Bank (PDB) crystal structure databases in order to understand the structural chemistry of calcium and identify geometrical features of a general nature.[2–5] In a pioneering study, Einspahr and Bugg[2] examined the crystal structures of sixty two crystalline hydrates of calcium and showed that calcium–water interactions involve factors that impose significant constraints on the geometries of these compounds. With respect to calcium–carboxylate interactions, Einspahr and Bugg[3] reported that the Ca ion in

all calcium-carboxylates lies near the plane of the carboxylate group and usually binds to several carboxylate groups. The most commonly observed number of carboxylates bound to each Ca was three and the carboxylate groups so bound may be crystallographically independent or symmetry related. It was also noted that the carboxylate groups coordinate to more than one Ca ion. Based on a study of protein crystal structures, Glusker and co-workers[4] reported that calcium has less affinity for water as compared to magnesium. Of the 187 small molecular crystal structures examined by the Glusker group, a majority (73%) of the Ca(II) compounds showed a Ca:water ratio of 1:3 or less. A recent study based on the analysis of the crystal structures of 131 Ca-carboxylates has shown that the coordination number of calcium ranges from three to ten, with octacoordination being the most favoured.[5] Due to the larger ionic radius of 106 pm for Ca^{2+}, the carboxylate ligand adopts a bridging binding mode resulting in the formation of a chain polymer in several structurally characterized calcium-carboxylates.[6–47] Based on an analysis of several calcium carboxylates it has been observed that, when the number of coordinated water molecules is three or less the carboxylate ligand exhibits a bridging binding mode.[36] Studies on the

carboxylates of Ca(II) based on amino acids [7–13,42–48] or hydroxy acids [5,49] have been reported.

In a recent paper, Strasdeit and co-workers have described laboratory experiments involving *s*-block metal chlorides and glycine, pertinent to the prebiotic hot volcanic scenario [12] and have shown that the calcium chloride–glycine–water system affords the isolation of three different Ca(II) compounds depending on reactant ratio and reaction conditions. In view of our longstanding interest on the structural aspects of metal–glycine compounds, [42–47] we have reinvestigated the calcium chloride:glycine:water system and have characterized a new Ca(II) coordination polymer in which a zwitterionic glycine functions as μ_3-bridging tetradentate ligand. The results of these investigations are described herein.

2. Experimental

2.1 *Materials and methods*

All the chemicals used in this study were of reagent grade and were used as received. The starting materials and reaction products were air stable and hence were prepared under normal laboratory conditions. The reported compound $[[Ca(H–gly)(H_2O)_3]Cl_2 \cdot H_2O]_n$ (**2**) was prepared following literature procedure. [42] Infrared (IR) spectra were recorded on a Shimadzu (IR prestige −21) FT-IR spectrometer in the range 4000–400 cm^{-1}. Samples for IR spectra were diluted with solid KBr and the signals referenced to polystyrene bands. UV-visible spectra were obtained using a Shimadzu UV-2450 double beam spectrophotometer.

2.2 *Synthesis of $[[Ca_6(H–gly)_{12}(H_2O)_{18}]Cl_{12} \cdot 6H_2O]_n$ (1)*

An aqueous solution containing calcium chloride dihydrate and glycine in 1:4 mol ratio was prepared. The reaction mixture was filtered and left undisturbed for crystallization. Slow evaporation at room temperature (27°C) resulted in the formation of transparent crystals in about a week's time in ∼20% yield.

Anal. Calcd. for $Ca_6C_{24}H_{108}Cl_{12}N_{12}O_{48}$ (1999.10) **1**: C, 14.42, H, 5.45, N, 8.41 Found: C, 14.52; H, 5.31; N, 8.38.

IR data: 3163, 3007, 2970, 2123, 1585, 1502, 1442, 1409, 1332, 1132, 1112, 1033, 910, 893, 698, 607, 503 cm^{-1}.

2.3 *X-ray crystal structure determination*

Intensity data for (**1**) were collected on Bruker SMART APEX CCD area-detector diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation. An empirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the coordinated and lattice water molecules could not be located. The hydrogen atoms attached to the C and N atoms of glycine were positioned with idealized geometry and refined using a riding model. Crystal data of (**1**) $C_{24}H_{108}Ca_6Cl_{12}N_{12}O_{48}$, M = 1999.10 g mol^{-1}, triclinic, space group = $P-1$, $\lambda = 0.71073$ Å, a = 14.702(1) Å, b = 15.483(1) Å, c = 18.824(2) Å, $\alpha = 88.96(1)°$, $\beta = 73.62(1)°$, $\gamma = 88.65(2)°$, V = 4109.9(6) Å^3, Z = 2, D$_{calc}$ = 1.615 mg m^{-3}, $\mu = 0.877$ mm^{-1}, F(000) = 2088, index range = $-1 \le$ h ≤ 17, $-18 \le$ k ≤ 18, $-21 \le$ l ≤ 22; completeness to theta = 25.0° (99.9%). A total of 16337 reflections ($2.02 < \theta < 25.0°$) were collected of which 14481 were unique (R$_{int}$ = 0.0091) and used for structure solution. Structure was solved using SHELXS-97[50] and refined using SHELXL-97[50] to R1 (wR2) = 0.0578 (0.1824) for 8770 reflections with (I > *2σ(I)*) using 931 parameters. Highest peak and deepest hole were observed at 1.093 and −0.870 eÅ^{-3}, respectively.

3. Results and discussion

3.1 *Synthetic aspects and spectral characteristics*

The calcium chloride–glycine–water system has been investigated by several research groups. [11,12,42,51–58] Although several different products containing calcium chloride, glycine and water are reported in the older literature, [51–58] the first structurally characterized compound in this series (table 1) containing a neutral zwitterionic glycine ligand $[[Ca(H–gly)(H_2O)_3]Cl_2 \cdot H_2O]_n$ (**2**) was reported by Natarajan and Rao. [42] Strasdeit and co-workers have recently isolated two more products from the calcium chloride–glycine–water system containing CaCl$_2$:glycine in a 1:1 ratio. [12] While a trihydrate CaCl$_2$·H–gly·3H$_2$O, [12] which exhibits a one-dimensional structure was obtained from an aqueous reaction mixture containing CaCl$_2$:glycine in a 5:1 ratio by slow evaporation of water in a desiccator over P$_2$O$_5$, a monohydrate CaCl$_2$·H–gly·H$_2$O [12] was isolated from an aqueous reaction mixture containing equimolar ratios of CaCl$_2$:glycine by rotary evaporation of the water at 50°C. The complex nature of the calcium chloride–glycine–water system can be evidenced from the fact that if the volume of the reaction mixture is reduced too much during the synthesis of the trihydrate, then the monohydrate also crystallizes. The trihydrate compound CaCl$_2$·H–gly·3H$_2$O has also been crystallized by slow evaporation of an aqueous solution having CaCl$_2$:glycine in a 1:1 ratio. [11] Recently

**Table 1.** Synthesis and structural aspects of CaX$_2$-H–gly compounds.

No	Compound	Reagents (ratio)	Method	Space group	Coord. sphere	Binding mode of glycine*	Ref
1	[[Ca$_6$(H–gly)$_{12}$(H$_2$O)$_{18}$]Cl$_{12}$·6H$_2$O]$_n$ (**1**)$^\varsigma$	CaCl$_2$:H–gly (1:4)	A	P-1	{CaO$_8$} {CaO$_8$} {CaO$_8$} {CaO$_8$} {CaO$_8$} {CaO$_8$}	Mode a (6)** Mode d (6)	This work
2	[[Ca(H–gly)(H$_2$O)$_3$]Cl$_2$·H$_2$O]$_n$ (**2**)	CaCl$_2$:H–gly (1:2)	A B	P2$_1$/c	{CaO$_8$}	Mode a (1) Mode d (1)	42 12
3	[CaCl(H–gly)$_3$]Cl	CaCl$_2$:H–gly (saturated solution)	A	Pb2$_1$a	{CaO$_6$Cl} {CaO$_6$Cl}	Mode a (2) Mode b (2) Mode c (2)	46
4	[CaCl(H–gly)(H$_2$O)$_3$]Cl	CaCl$_2$:H–gly (1:1) CaCl$_2$:H–gly (5:1) CaCl$_2$:H–gly (1:1)	A C D	P2$_1$/c	{CaO$_7$Cl}	Mode d (1)	11,12
5	[CaCl$_2$(H–gly)(H$_2$O)]$^\#$			–	–	–	12
6	[Ca(NO$_3$)(H–gly)(H$_2$O$_2$)](NO$_3$)	Ca(NO$_3$)$_2$:H–gly (1:1)	A	P2$_1$2$_1$2$_1$	{CaO$_8$}	Mode d (1)	45
7	CaBr(H–gly)$_3$]Br	CaBr$_2$:H–gly (saturated solution)	A	Pbc2$_1$	{CaO$_6$Br} {CaO$_6$Br}	Mode a (2) Mode b (2) Mode c (2)	43
8	[Ca(H–gly)$_3$(H$_2$O)]I$_2$	CaI$_2$:H–gly (saturated solution)	A	P2$_1$/c	{CaO$_7$}	Mode a (1) Mode b (1) Mode e (1)	44
9	[[Ca(H–gly)$_2$(H$_2$O)$_3$]I$_2$]$_n$	CaI$_2$:H–gly (1:2)	A	Pca2$_1$	{CaO$_7$} {CaO$_7$}	Mode b (4)	11,47
10	[Ca(H–gly)$_2$(H$_2$O)$_4$]Br$_2$]$^\$$	–	–	P2$_1$/c	–	–	61
11	[Ca(gly)$_2$(H$_2$O)]	Ca(OH)$_2$:H–gly (1:1)	E	P-1	{CaN$_2$O$_6$}	Mode f (1) Mode g (1)	13

Abbreviations used Method A = Slow evaporation; Method B = Rotary evaporation followed by slow evaporation; Method C = Slow evaporation over P$_2$O$_5$; Method D = Rotary evaporation at 50°C; Method E = Reflux in water; ς Compounds **1** and **2** have the same composition; # Characterized by analytical and spectral data and powder diffraction. $ Only unit cell reported; atom coordinates and synthetic method are not given. * For binding mode see figure 4. ** Number in bracket indicates the number of independent H–gly ligands

we have shown that slow evaporation of an aqueous reaction of equimolar ratios of $SrCl_2$ and glycine results in the formation of a chloride coordinated Sr compound $[Sr(H–gly)_2(H_2O)Cl_2]_n$ in low yield,[59] containing Sr:glycine:water in a 1:2:1 mol ratio, in contrast to the earlier reported synthesis of a trihydrate compound $[Sr(H–gly)_2(H_2O)_3]Cl_2$ containing uncoordinated chlo-

ride crystallized from an aqueous solution containing $SrCl_2$ and glycine in a 1:2 mol ratio.[60] It is to be noted that for all our reported work in this area so far, we have employed the method of slow evaporation at room temperature for product isolation, from a reaction mixture containing a fixed stoichiometry of metal salt and glycine or a saturated solution of glycine in
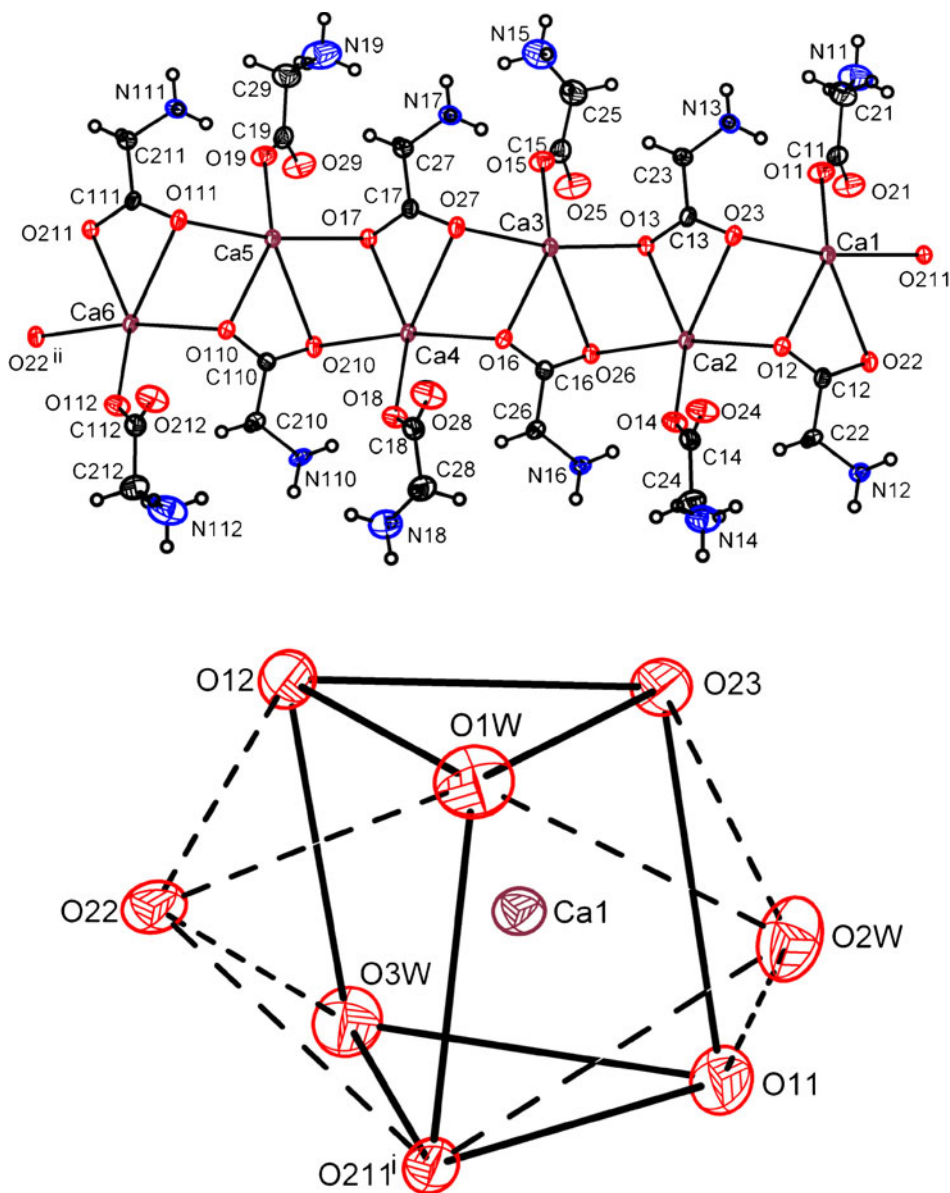
Figure 1. The crystal structure of (**1**) showing the atom labelling scheme. Only the twelve unique glycine ligands coordinated to the six independent Ca(II) in compound (**1**) are shown (top). Thermal ellipsoids are drawn at the 50% probability level excepting for H atoms of glycine, which are shown as circles of arbitrary radius. For clarity, the terminal water molecules (O1W to O18W) around each Ca, the chloride anions (Cl1 to Cl12) and the lattice water molecules (O19W to O24W) are not shown. The distorted bicapped trigonal prismatic coordination environment of Ca1. The atoms O22 and O2W on the rectangular faces of the trigonal prism function as capping atoms (bottom). Symmetry codes: i) x+1, y, z−1; ii) x−1, y, z+1.

which metal salt is added to achieve metal saturation. Since reaction mixtures rich in CaCl$_2$ result in a 1:1 (Ca:H–gly) product[12] it was of interest to study products from reaction mixtures containing excess glycine. In this work, we have investigated the aqueous reaction of CaCl$_2$:glycine in a 1:4 mol ratio by the slow evaporation method. The analytical data of the product (**1**) showed a Ca:glycine in a 1:2 ratio. Interestingly, the composition of (**1**) obtained from the 1:4 reaction of CaCl$_2$:glycine was identical to that of the previously reported compound [[Ca(H–gly)(H$_2$O)$_3$]Cl$_2$·H$_2$O]$_n$ (**2**) obtained by the slow evaporation method from a 1:2 reaction of CaCl$_2$:glycine. However, the X-ray powder pattern (figure S1) of (**1**) was different from that of (**2**) clearly indicating the formation of a new phase, which was unambiguously confirmed by its crystal structure determination (*vide infra*).

Compound **1** does not show any absorption signals in its UV-Vis spectrum. The IR spectrum of **1** exhibits several signals in the mid IR region, indicating the presence of the organic moiety. A comparison of the IR spectra of pure glycine and the title compound (figure S2) shows the observation of a broad and strong band between 3500 and 2500 cm^{-1}, which can be attributed to the presence of water in **1**. The IR spectrum of (**1**) is very similar to that of (**2**). In the carboxylate region the band

at 1665 cm^{-1} in free glycine is shifted to 1585 cm^{-1} in **1**. Although the several signals do indicate the presence of organic moiety, the exact nature of the binding mode of the glycine ligand cannot be inferred from infrared data alone.

3.2 *Crystal structure description of [[Ca$_6$(H–gly)$_{12}$(H$_2$O)$_{18}$]Cl$_{12}$·6H$_2$O]$_n$ (1)*

Compound **1** crystallizes in the centrosymmetric triclinic space group *P-1* with all atoms situated in general positions. The crystal structure of **1** consists of six crystallographically independent Ca(II) ions, twelve unique glycine molecules, twelve independent chloride anions, eighteen unique terminal water molecules and six independent lattice water molecules (figure 1 and figure S3). All the twelve unique glycine molecules are in their zwitterionic form and can be classified into two types namely, six μ$_3$-bridging tetradentate ligands and six monodentate glycine ligands. The geometric parameters of the glycine ligands are in the normal range. Each Ca(II) is bonded to three terminal water molecules, one monodentate glycine and four oxygen atoms from three symmetry related μ$_3$-bridging tetradentate glycine ligands. The coordination sphere around all the six unique Ca(II) ions, which exhibit

Table 2. Selected metric parameters (Å, °) for [[Ca$_6$(H–gly)$_{12}$(H$_2$O)$_{18}$]Cl$_{12}$·6H$_2$O]$_n$ (**1**).

Bond distances

Ca(1)-O(23)	2.354(3)	Ca(1)-O(11)	2.422(3)
Ca(1)-O(211)^i	2.357(3)	Ca(1)-O(3W)	2.454(3)
Ca(1)-O(1W)	2.414(3)	Ca(1)-O(12)	2.518(3)
Ca(1)-O(2W)	2.418(3)	Ca(1)-O(22)	2.830(3)

Bond angles

O(23)-Ca(1)-O(211)^i	168.32(9)	O(11)-Ca(1)-O(3W)	73.89(9)
O(23)-Ca(1)-O(1W)	103.22(10)	O(23)-Ca(1)-O(12)	75.16(9)
O(211)^i-Ca(1)-O(1W)	81.70(10)	O(211)^i-Ca(1)-O(12)	116.50(9)
O(23)-Ca(1)-O(2W)	86.33(10)	O(1W)-Ca(1)-O(12)	74.46(9)
O(211)^i-Ca(1)-O(2W)	85.15(10)	O(2W)-Ca(1)-O(12)	136.51(10)
O(1W)-Ca(1)-O(2W)	72.03(10)	O(11)-Ca(1)-O(12)	138.16(9)
O(23)-Ca(1)-O(11)	78.97(9)	O(3W)-Ca(1)-O(12)	76.60(9)
O(211)^i-Ca(1)-O(11)	90.85(9)	O(23)-Ca(1)-O(22)	123.03(8)
O(1W)-Ca(1)-O(11)	144.27(10)	O(211)^i-Ca(1)-O(22)	68.50(8)
O(2W)-Ca(1)-O(11)	72.54(9)	O(1W)-Ca(1)-O(22)	71.05(9)
O(23)-Ca(1)-O(3W)	95.71(10)	O(2W)-Ca(1)-O(22)	137.02(9)
O(211)^i-Ca(1)-O(3W)	86.82(10)	O(11)-Ca(1)-O(22)	137.82(9)
O(1W)-Ca(1)-O(3W)	139.70(10)	O(3W)-Ca(1)-O(22)	68.80(9)
O(2W)-Ca(1)-O(3W)	145.31(10)	O(12)-Ca(1)-O(22)	48.23(8)

Note – Symmetry transformations used to generate equivalent atoms: i) x+1, y, z−1; For metric parameters of the other unique Ca(II) ions namely Ca(2) to Ca(6), see Supplementary tables S1 and S2

eight coordination are identical and hence the structure is explained for one of the six unique Ca(II) ions namely Ca1. Each unique Ca(II) is bound to eight oxygen atoms and the coordination polyhedron around Ca is perhaps best described as a distorted trigonal prism that has two of its rectangular faces capped. In Ca1, the atoms O22 and O2W on the rectangular faces function as capping atoms (figure 1). The Ca–O bond distances vary between 2.354(3) and 2.830(3) Å (table 2) for Ca1 and are in agreement with reported data.[12,42–47] Of the eight Ca–O distances for each unique Ca, three are due to those of the terminal water ligands. For Ca1 the three terminal Ca–O(water) distances are in a very narrow range between 2.414(3) and 2.454(3) Å and the Ca1–O11 distance due to the monodentate glycine is observed at 2.422(3) Å (see figure S4). The μ_3-bridging tetradentate glycine ligand (O12, O22) is linked to Ca1

at longer distances of 2.517(3) and 2.830(3) Å, respectively (figure 2). The O12 is further bonded to Ca2 at 2.354(3) Å with a Ca1···Ca2 separation of 4.042(1) Å while the O22 is linked to Ca6 at 2.344(3) resulting in a Ca1···Ca6 distance of 4.052(2) Å.

The Ca–O distances for the other unique Ca atoms namely Ca2 to Ca6 are in the same range as for Ca1 (table S1) and can be explained similarly (see figure S5). The O–Ca–O angles scatter in a very wide range and for Ca1 the values range from 48.23(8) to 168.32(9)° (table 2). The O–Ca–O angles for the other five unique Ca atoms are also in the same range as for Ca1 (table S2). The net result of the μ_3-bridging tetradentate binding mode of the glycine ligands is the formation of a one-dimensional coordination polymer (figure 3) with six different Ca···Ca separations of 4.042(1), 4.037(2), 4.053(1), 4.052(2), 4.049(1) and
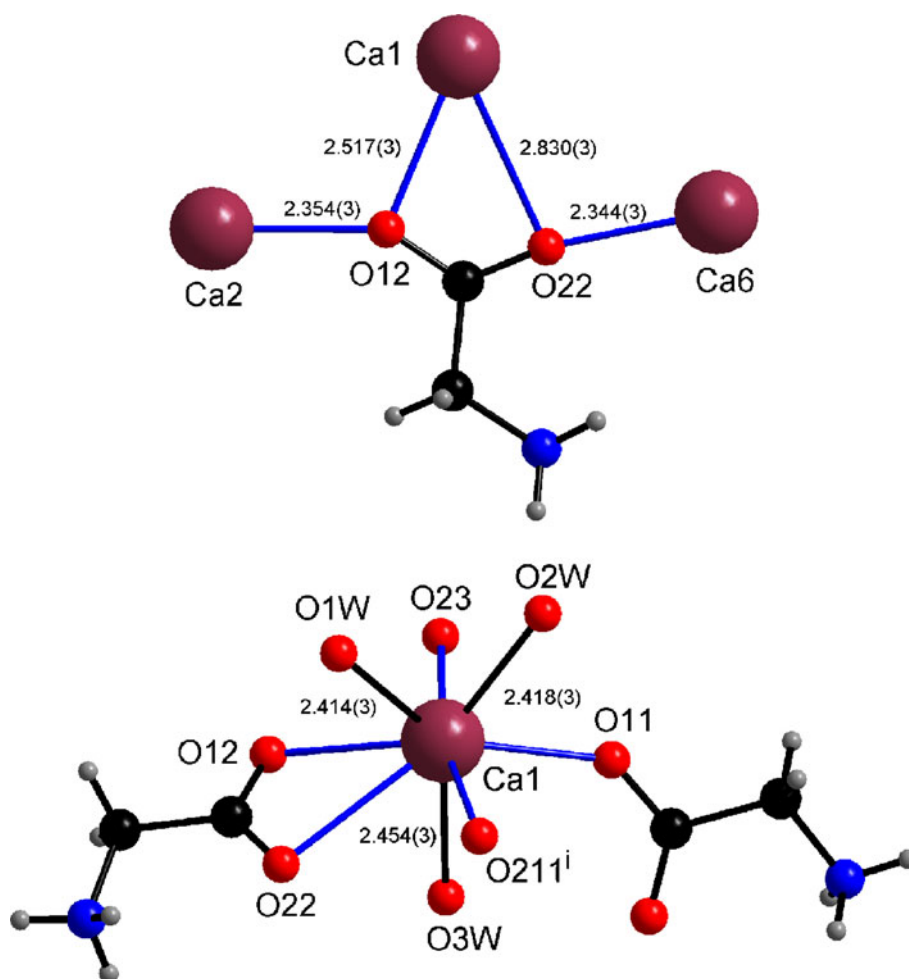
Figure 2. The μ_3-bridging tetradentate binding mode of one of the unique glycine (O12, O22) ligands, showing the four Ca–O bonds in blue (top). The octa coordination around Ca1. O1W, O2W and O3W are terminal water molecules and the Ca–O (water) bond is shown in black. O11 is monodentate glycine while O211 and O23 are from symmetry related bridging glycine ligands. The five Ca–O (glycine) bonds are shown in blue.
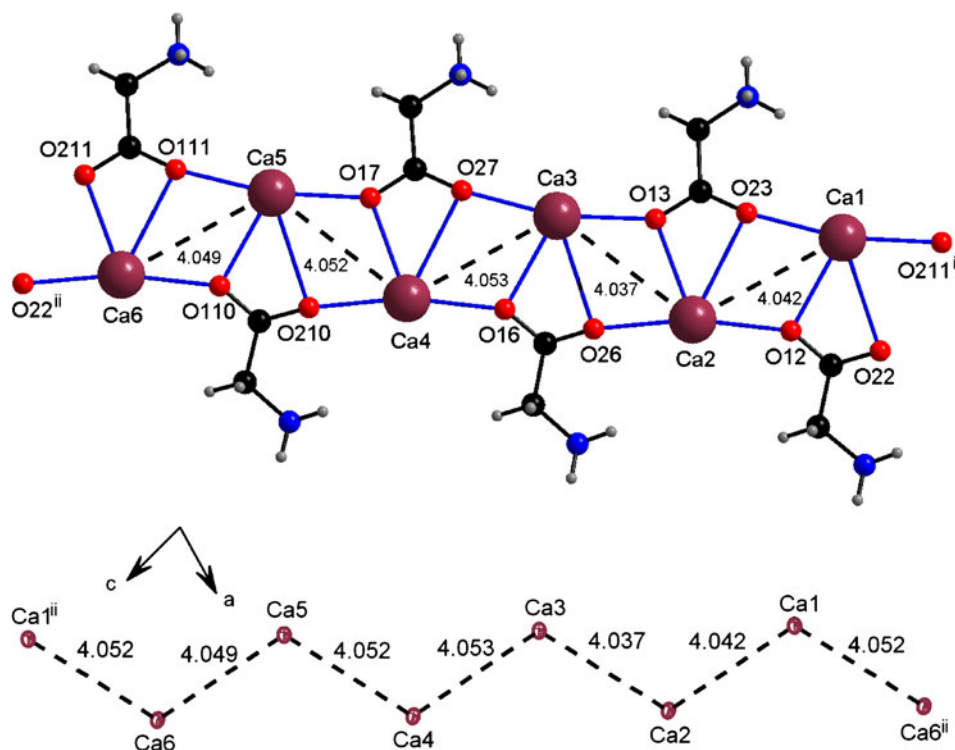
Figure 3. A portion of the structure showing only the μ_3-bridging tetradentate glycine ligands leading to the formation of a one-dimensional coordination polymer (top). The Ca–O bonds are drawn in blue. In the polymeric chain extending along c axis the Ca$\cdots$Ca separations are longer than 4.0 Å. For clarity, the three coordinated water molecules and the monodentate glycine ligands around Ca(II) are not shown. A portion of the zig zag calcium chain (bottom).

4.052(2) Å, respectively. In the polymeric chain each, unique Ca is bonded to four different glycine ligands one of which is a monodentate glycine and the other three are bridging ligands. The Ca atoms are organized in a zigzag fashion in the infinite chain (figure 3). The crystal structure reveals that H atoms attached to the N atoms of the unique zwitterionic glycine ligands are involved in several N–H$\cdots$Cl and N–H$\cdots$O interactions (see table S3) with the chloride anions and the oxygen atoms of the carboxylate group of the glycine functioning as H-acceptors. As the H atoms attached to the coordinated and lattice water molecules could not be located, a detailed description of the secondary interactions in **1** is not given.

3.3 *Structural aspects of calcium halide – glycine compounds*

The freely water soluble achiral amino acid glycine (H–gly) functions as a O-donor and not N-donor ligand in its neutral zwitterionic form and is thus a suitable ligand for the oxophilic *s*-block metal cations. In an alkaline medium H–gly forms the glycinate anion

(gly)$^-$ and can function as an anionic ligand. From a structural point of view glycine is a stereochemically flexible molecule and can bind to metals as a monodentate or a bidentate or bridging ligand. Although binding through both N and O atoms are conceivable, glycine functions as an O donor ligand in its neutral zwitterionic form. Unlike the zwitterionic H–gly where the N atom is protonated, the lone pair on N is available for coordination in the glycinate anion. Of the several metal, halogenide compounds containing neutral zwitterionic glycine ligands bonded to several metal cations reported in the literature[61] the calcium halide–glycine compounds (table 1) constitute a unique group because Ca(II) forms the maximum number ($\sim$25%) of compounds with glycine. One example of a calcium *bis*(glycinate) compound[13] (entry no. 11) has been reported. Based on a study of about thirty five crystal structures containing glycine, metal cations and halogenide ions Fleck[61] has recently reported that the percentage (28%) of non-centrosymmetric structures in this class of compounds is high and much more than the usual 15%. In the group of calcium halide–glycine compounds four out of ten compounds (40%) crystallize in non-centrosymmetric space groups.
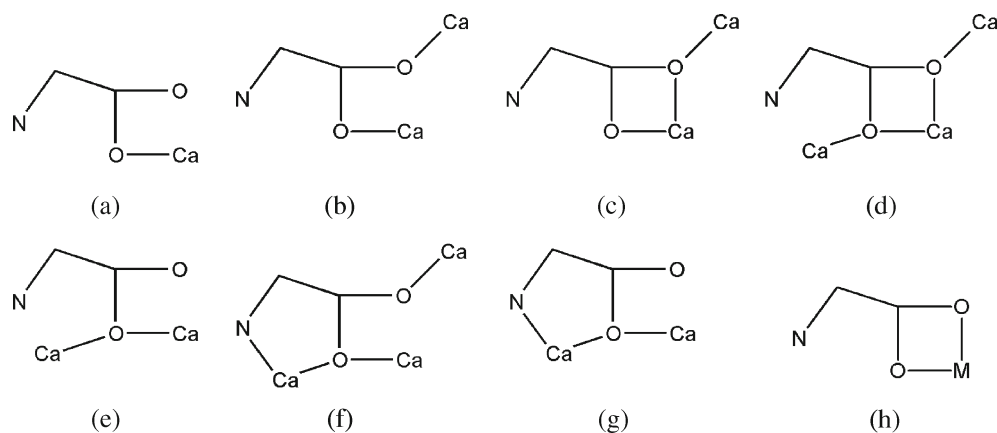
Figure 4. Binding modes of H–gly (mode a to e) or (gly)⁻ (mode f and g) in calcium–glycine compounds. H atoms are not shown. Mode a – monodentate (O); Mode b – symmetric bridging (O, O'); Mode c – μ_2-bridging tridentate (O, O, O'); Mode d – μ_3-bridging tetradentate (O, O, O', O'); Mode e – asymmetric bridging (O, O); Mode f – μ_3-bridging tetradentate (O, O, O', N) and Mode g – μ_2-bridging tridentate (O, O, N); Mode h – bidentate (O,O').

In these compounds, the central metal adopts either eight (ten Ca(II) sites) or seven (seven Ca(II) sites) coordination. The preference for eight coordination is in accordance with literature report.[5] In these compounds the zwitterionic glycine exhibits a total of five different binding modes (figure 4), four of which (mode b to mode e) are bridging coordination modes. It is to be noted that the μ_3- and μ_2-bridging binding modes of the glycinate anion involve N atoms (mode f and mode g) and are different from those of the corresponding μ_3- and μ_2-bridging modes (mode d and mode c). The bridging binding modes of H–gly results in the formation of a polymeric chain structure. It is interesting to note that all structurally characterized Ca(II) compounds listed in table 1 exhibit at least one bridging binding mode and are one-dimensional coordination polymers excepting the anhydrous compounds [CaCl(H–gly)₃]Cl and its bromide analog (entry no. 3 and 7 in table 1) which are two-dimensional polymers. Both the anhydrous calcium halogenide–glycine compounds contain six unique H–gly ligands four of which are bridging in nature. It is observed that the pure bidentate mode (mode h) and also coordination of N atom is not observed in any of the calcium–halide glycine compounds. A comparison of compound **1** with other eight coordinated Ca–glycine compounds like [CaCl₂(H–gly)(H₂O)₃], [[Ca(H–gly)(H₂O)₃]Cl₂·H₂O]ₙ and [Ca(gly)₂(H₂O)] indicates certain interesting structural features. Both the 1:1 Ca:glycine compound [CaCl₂(H–gly)(H₂O)₃][11,12] and the 1:2 compound [[Ca(H–gly)(H₂O)₃]Cl₂·H₂O]ₙ contain a μ_3-bridging tetradentate glycine ligand. The 1:1 compound which has a {CaO₇Cl} coordination sphere is identical with **1** but for the Cl ligation to Ca instead of the monoden-

tate glycine in **1**. It is to be noted that the environment of Ca(II) in compound **1** is identical to that of the earlier reported[42] one-dimensional polymeric compound [[Ca(H–gly)(H₂O)₃]Cl₂·H₂O]ₙ which crystallizes in the monoclinic $P2_1/c$ space group. However, this compound differs from compound **1** and in that it exhibits a single unique Ca···Ca separation instead of six distinct Ca···Ca separations in **1**. The eight coordinated Ca compound [Ca(gly)₂(H₂O)] obtained by reaction of Ca(OH)₂ with glycine contains glycinate anion for charge balance instead of Cl⁻ ions and in this compound the N of glycinate is also coordinated to Ca. It is to be noted that when CaBr₂ or CaI₂ are used instead of CaCl₂, the bromide ion is bonded to Ca but not iodide and these compounds exhibit hepta coordination.

4. Conclusions

In summary, we have described the synthesis, spectral and structural characterization of a new coordination polymer of Ca(II) containing a μ_3-bridging tetradentate zwitterionic glycine ligand. A comparative study reveals a rich and variable structural chemistry of calcium halide–glycine compounds. The polymeric compound (**1**) reported here is a new example to the growing list of structurally characterized calcium coordination polymers.

Supplementary material

Crystallographic data (excluding structure factors) for the structure of compound **1** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.

CCDC 828382. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

For tables S1–S3 and figures S1–S5, see the website (www.ias.ac.in/chemsci).

Acknowledgements

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