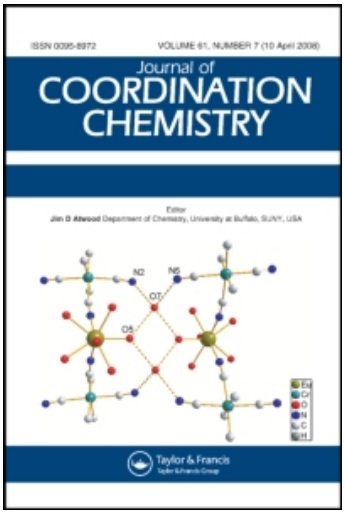

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Structural determination and characterization of copper and zinc *bis*-glycinates with X-ray crystallography and mass spectrometry

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X-ray crystallography, inductively coupled plasma spectroscopy, electrospray mass spectroscopy, and combustion elemental analysis were used to determine the content and structure of copper and zinc *bis*-glycinate crystals. Crystals were grown from copper sulfate-glycine and zinc hydroxide-glycine solutions. The crystal structures were then resolved by X-ray crystallography, and data from electrospray mass spectroscopy along with elemental analyses are used to support the crystal structure. The copper compound consists of Cu chelated by two glycinate units in a *cis* configuration. A water molecule bonds to Cu forming a distorted square pyramid. These units are bonded through the free carboxylate oxygens into polymeric chains that are in turn connected through hydrogen bonds. In contrast, the zinc compound, while also chelated by two glycine units, has a *trans* configuration. These units are bonded together into tetra-zinc glycinate clusters by bonding to carboxylate oxygens creating distorted metal square pyramid coordination polyhedra. The mass spectra confirm the polymeric nature of the metal glycinates.

Keywords: Metal glycinates; Crystal structures; Electrospray mass spectroscopy

1. Introduction

At the beginning of the twentieth century, animals were fed controlled diets containing purified proteins, fats, carbohydrates, and inorganic salts of minerals. It was found that these animals would thrive on this controlled diet only when small amounts of milk were added to it. This experiment was the first of many which laid the foundation for what we know as food fortification and the later development of modern nutrition [1]. In 1939, with the advent of analytical procedures using emission spectroscopy, the essential nature of minerals in the diet was gaining acceptance [2]. Treating diseases and increasing production with trace and macro minerals date from antiquity. As early as 29 AD, animals were fed salts for milk production [3].

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Since the early discovery of vitamins and minerals as nutritional factors, there have been many advances in the quality and availability of these nutritional factors. It has been found that merely supplying essential nutrients is not always adequate. There are many forms of minerals which can be administered [4]. Advances have been made with respect to metal–organic compounds that are absorbed and assimilated better than traditional inorganic salts. One example of a class of such compounds that provide better absorption than traditional inorganic salts is that of metal amino acid chelates. Ashmead *et al.* were among the first to demonstrate improved bioavailability of metal amino acid chelates in plant, animal, and human nutrition models [5, 6]. The use of metal amino acid chelates is common in today's marketplace [7, 8]. With rapidly growing sales, popularity, and tighter government regulations, a need has been created to better understand the chemical composition and structure of metal amino acid chelates. In this article, we have characterized the crystal structure, carbon, nitrogen, and metal content of copper and zinc *bis*-glycinates by making use of X-ray crystallography, inductively coupled plasma atomic emission spectroscopy, electrospray mass spectroscopy, and combustion elemental analysis.

The crystal structure of the copper glycinate was first determined from Weissenberg projection data by Tomita and Nitta [9]. This structure was later refined by a joint effort between these authors and Freeman and Snow [10]. The refinement of the data was carried out by a 3-D least-squares method. In this study, it was found that larger crystals more suitable for single crystal studies were obtained if triglycine was present in the preparation solution. The crystal data are presented in table 1. These authors considered the compound to consist of five-coordinate copper as shown in figure 1 with nitrogens *cis*. However, a non-bonded carboxyl oxygen was found at 2.74 Å from the Cu as a weak bond tying the copper glycinate groups into chains.

Subsequently, Moussa *et al.* [11] were able to prepare the *trans* form by heating the *cis* form in excess glycine. It is monoclinic, $I2/a$; $a = 9.6566(8)$, $b = 5.2410(7)$, $c = 14.836(1)$ Å, $\beta = 92.764(8)$ Å, and $V = 750.85$ Å^3. They also prepared the anhydrous derivatives of the *cis*- and *trans*-glycinate phases. Subsequently, they were able to solve the structure of these phases by a combination of X-ray and neutron powder data [12].

A final redetermination of the *cis*-phase was carried out by Casari *et al.* [13]. The unit cell dimensions of these literature structures are collected in table 2. Even with modern equipment and software, there is still a difference in the unit cell dimensions that shows up in the volumes between the MFK and CML papers (table 2) partly due to the different temperatures at which the data were obtained. Our purpose in redoing the copper structure was to illustrate the polymer nature of the compound pictorially and the justification for the observed mass spectrometry data.

Two earlier references to the crystal structure of zinc and cadmium glycinates were found in the Cambridge Data Base. Low *et al.* [14] prepared the zinc and cadmium glycinates by reaction of the metal oxides with glycine in boiling water. Flat platelets were obtained for the Zn compound, space group $P\bar{1}$ with $a = 15.051$, $b = 10.441$, $c = 11.153$ Å, $\alpha = 118.02°$, $\beta = 92.51°$, and $\gamma = 90.39°$ with eight molecules per unit cell. They also indicated that the glycine atoms formed a square planar arrangement but that free carboxylate oxygens filled axial sites, creating Zn octahedra. Many textbooks still attribute this structure as correct. However, the presence of eight molecules in a triclinic unit cell is very unlikely. It is obvious that these authors used the wrong space group and could only arrive at a tentative solution.

Table 1. Crystallographic data for copper and zinc glycinates.

	1	**2**
Empirical formula	$CuC_4H_{10}N_2O_5$	$Zn_4C_{16}H_{40}N_8O_{20}$
Formula weight (g)	229.68	926.096
Color, habit	Blue, needles	Colorless plates
Temperature (K)	110(2)	113(2)
Wavelength λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$
Unit cell dimensions (Å, °)		
a	5.204(1)	19.694(4)
b	10.709(2)	10.420(2)
c	13.539(3)	14.915(3)
α	90	90
β	90	92.68(3)
γ	90	90
Volume (Å^3), Z	754.7(3), 4	3057.4(11), 4
Calculated density ρ (g cm^{-3})	2.021	2.012
Absorption coefficient μ (mm^{-1})	2.879	3.2
$F(000)$	468	1888
Crystal size (mm^3)	$0.3 \times 0.05 \times 0.02$	$0.35 \times 0.25 \times 0.1$
θ range for data collection (°)	2.42–29.71	2.57–27.35
Reflections measured	8357	9792/0.0382
Data/R(int)/parameters	1738/0.0579/122	2672/0.0377/240
Goodness-of-fit on F^2	1.005	1.05
Final R indices [$I > 2.0\sigma(I)$]	$R_1 = 0.0234$, $wR_2 = 0.0537$	$R_1 = 0.0614$, $wR_2 = 0.1385$
R indices (all data)	$R_1 = 0.0268$, $wR_2 = 0.0551$	$R_1 = 0.0771$, $wR_2 = 0.1468$

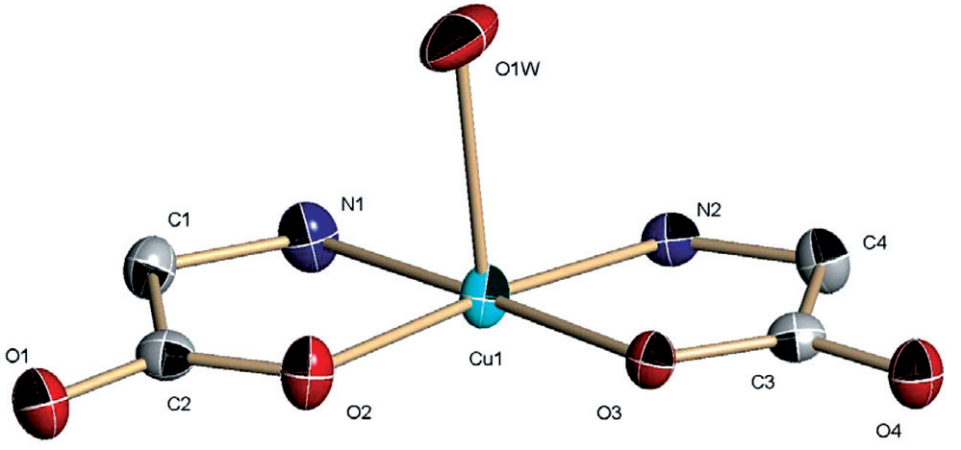

Figure 1. ORTEP representation at the 50% probability level of a molecule of copper glycinate together with the numbering scheme used in the structure solution. Color scheme: Cu, blue; O, red; N, violet; and C, gray. Hydrogens omitted for clarity.

This structure was redone by Newman *et al.* [15]. They also indicated a space group of $P\bar{1}$ but with different cell parameters: $a = 9.165(7)$, $b = 9.571(7)$, $c = 10.438(9)$ Å, $\alpha = 105.97(4)°$, $\beta = 106.19(4)°$, and $\gamma = 107.12(4)°$, with four molecules per unit cell. The authors indicated that good crystals were difficult to grow and there was disorder

Table 2. Unit cell dimensions and crystal data for copper glycinate, $CuC_4H_8N_2O_4 \cdot H_2O$.

	TN[9]	FS[10]	MFK[11]	CML[13]
λ (Å)	1.542	1.5418	1.5418	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions (Å, °)				
a	10.78(1)	10.866(17)	10.8095(9)	5.1920(3)
b	5.2089(4)	5.220(7)	5.2165(5)	10.6850(6)
c	13.47(2)	13.502(21)	13.503(1)	13.5535(8)
α, β, γ	90	90	90	90
V (Å^3)	756.5	765.9	761.4	751.90(8)

of the Zn. Apparently, they were dealing with twinned crystals. They concluded that the coordination of zinc was five with bond angles between those of a square pyramid and a trigonal bipyramid. Our results for Zn are quite different from these earlier studies.

2. Experimental sample preparation

2.1. *Copper glycinate*

Glycine (3.75 g, 0.05 mol L^{-1}) was dissolved in 200 mL of water at ~20°C. Copper sulfate pentahydrate (6.24 g, 0.025 mol L^{-1}) was dissolved in 200 mL of water and added slowly to the glycine solution. The solution pH was adjusted to 7.0 with a dilute NaOH solution and allowed to stand at room temperature (~20°C) for 1 week. Bright blue crystals formed that were recovered by filtration and washed with a minimal amount of cold deionized water. Found: Cu, 30.77; C, 21.19; N, 11.78. Calculated for $Cu(C_2H_4NO_2)_2 \cdot H_2O$: Cu, 27.91; C, 21.10; N, 12.20.

2.2. *Zinc glycinate*

The zinc glycinate was prepared in a similar fashion as the copper compound using $Zn(OH)_2$ added to a hot glycine solution. The solution was allowed to stand overnight and then the liquid was reduced to half its volume in a rotary evaporator. The solid was filtered off and washed with small amounts of chilled non-denatured ethanol. The recovered solid was then redissolved in distilled water and non-denatured alcohol added to the extent of 10% of the solution volume. This solution was then kept in the refrigerator overnight. If suitable crystals were not obtained in a week's time, the solid was redissolved in a 2 : 1 distilled water–ethanol mixture, filtered to remove undissolved material and refrigerated. Suitable crystals were obtained by slow evaporation. Found: Zn, 31.20; C, 21.22; N, 11.88. Calculated for $Zn(O_2CCH_2NH_2)_2 \cdot H_2O$: 28.25; C, 20.75; N, 12.10.

Table 3. Bond lengths (Å) and angles (°) for copper glycinate.

Cu(1)–O(2)	1.9559(17)	C(2)–O(1)	1.245(3)
Cu(1)–O(3)	1.9606(17)	C(2)–O(2)	1.276(3)
Cu(1)–N(2)	1.9937(19)	C(3)–O(3)	1.275(3)
Cu(1)–N(1)	2.009(2)	C(3)–O(4)	1.240(3)
Cu(1)–O(1W)	2.376(2)	C(1)–C(2)	1.525(3)
C(1)–N(1)	1.468(3)	C(3)–C(4)	1.525(3)
C(4)–N(2)	1.467(3)	Cu(1)–O(4)A	2.667(5)
O(2)–Cu(1)–O(3)	93.16(7)	C(3)–O(3)–Cu(1)	115.6(2)
O(2)–Cu(1)–N(2)	174.63(9)	C(2)–O(2)–Cu(1)	115.7(2)
O(3)–Cu(1)–N(1)	84.89(7)	C(4)–N(2)–Cu(1)	110.0(2)
O(2)–Cu(1)–N(1)	84.79(8)	C(1)–N(1)–Cu(1)	109.7(2)
O(3)–Cu(1)–N(1)	177.78(9)	O(4)–C(3)–O(3)	124.0(2)
N(2)–Cu(1)–N(1)	97.08(8)	O(1)–C(2)–O(2)	123.7(2)
O(2)–Cu(1)–O–(1W)	88.95(10)	O(4)–C(3)–C(4)	118.8(2)
O(3)–Cu(1)–O(1W)	91.44(8)	O(2)–C(2)–C(1)	118.8(2)
N(2)–Cu(1)–O(1W)	96.10(10)	O(3)–C(3)–C(4)	117.2(2)
N(1)–Cu(1)–O(1W)	89.38(9)	O(2)–C(2)–C(1)	117.6(2)
		C(3)–C(4)–N(2)	118.9(2)
		C(2)–C(1)–N(1)	111.7(2)

2.3. *Crystallography*

A needle-shaped bright blue crystal of the copper glycinate mounted on a hollow glass tube was cooled to 110 K on a Bruker Smart CCD-1000 diffractometer using a cold nitrogen stream (Oxford). Data were collected with Mo-Kα radiation ($\lambda = 0.71073$ Å) every 0.3°. Thirty frames were rerun at the end of data collection to determine whether crystal deterioration had occurred. Data reduction and cell refinement were performed with the SAINT Program [16] and the absorption correction program SADABS [17] was utilized to correct for absorption effects. Crystal structures were solved by direct methods and refined with anisotropic thermal factors utilizing the full-matrix least squares program SHELXL-97 [18] for all non-hydrogen atoms. The positions of the hydrogens were calculated at 0.92 Å bond distance and assigned temperature factors one unit higher than the atoms to which they are bonded. A needle-shaped, colorless crystal of the zinc glycinate was treated similarly to that described for the copper compound. Significant disorder of the Zn atoms was found in the zinc glycinate crystals. Four different crystals were examined and all showed the same disorder. The nature of this disorder will be described later in the text.

The crystallographic data are summarized in table 1, important bond distances and angles are presented in tables 3 and 4, and other pertinent data have been deposited as supporting information.

2.4. *Mass spectrometry*

Mass spectra were collected with a Quattro-II mass spectrometer (Micromass, Inc.) equipped with electrospray ionization. Spectra were acquired in positive-ion mode over the mass range 50 to 950 m/z at a spray voltage of 2.8 kV and with a cone voltage of 25 eV. Samples were dissolved into nanopure water with 5% methanol and infused directly into the instrument at a flow rate of 3 μL min^{-1}. The sample concentration and ionization conditions were optimized for analysis of the protonated molecular ion of

Table 4. Bond lengths (Å) and angles (°) for zinc glycinate.

Zn1–O6	2.011(5)	C2–O1	1.271(8)
Zn1–N1	2.023(6)	C2–O2	1.242(8)
Zn1–N2	2.035(5)	C1–O2	1.512(6)
Zn1–O1	2.114(4)	C1–N1	1.476(8)
Zn1–O3	2.174(5)	C4–O3	1.252(8)
Zn2–N4	1.973(6)	C4–O4	1.265(8)
Zn2–N3	2.070(6)	C3–C4	1.516(6)
Zn2–O7	2.130(5)	C3–N2	1.475(8)
Zn2–O5	2.160(5)	C6–O5	1.238(8)
Zn2–O4	2.040(5)	C6–O6	1.271(8)
Zn3–N3	1.787(7)	C5–C6	1.512(6)
Zn3–N4	2.104(6)	C5–N3	1.463(8)
Zn3–O7	2.164(6)	C8–O7	1.264(8)
Zn3–O2	2.308(7)	C8–O8	1.243(8)
Zn3–O5	2.336(6)	C7–C8	1.515(6)
		C7–N4	1.474(8)
O(1)–Zn(1)–O(3)	161.7(2)	O(6)–Zn(1)–N(1)	111.5(2)
N(1)–Zn(1)–N(2)	138.7(2)	O(6)–Zn(1)–N(2)	109.2(2)
O(5)–Zn(2)–O(7)	160.3(2)	O(6)–Zn(1)–O(1)	103.2(2)
N(3)–Zn(2)–N(4)	139.6(3)	O(6)–Zn(1)–O(3)	94.8(2)
O(1)–Zn(1)–N(1)	80.7(2)	C(6)–O(6)–Zn(1)	119.8(4)
O(3)–Zn(1)–N(2)	80.4(2)	C(4)–O(4)–Zn(2)	124.1(4)
O(1)–Zn(1)–N(2)	96.7(2)	O(2)–C(2)–O(1)	124.4(6)
O(3)–Zn(1)–N(1)	89.7(2)	O(2)–C(2)–C(1)	117.4(6)
Zn(1)–O(1)–C(2)	113.5(4)	O(2)–C(2)–C(1)	118.2(6)
Zn(1)–N(1)–C(1)	111.8(4)	C(2)–C(1)–N(1)	112.0(5)

zinc *bis*-glycinate at 213 m/z (MH^+). The same conditions were used to analyze the copper *bis*-glycinate.

3. Results

3.1. *Copper glycinate crystal structure*

The prevailing motif in copper glycinate, showing the numbering scheme used in this study and the thermal ellipsoids, is given in figure 1. Important bond distances and angles are provided in table 3. Two glycinate ligands chelate the copper through nitrogen and one carboxylate oxygen. The arrangement of the ligands is *cis* with both nitrogens on the same side. The two oxygens and two nitrogens form a square plane and a water molecule in the axial position converts the geometry to a square pyramid. This water molecule-Cu bond length is 2.376(2) Å as compared to the average Cu–O bond distance 1.958 Å and the average Cu–N bond distance 2.001 Å (table 3). The coordination sphere is completed by a carboxyl oxygen, O4, bonding to Cu on the axial position opposite the water molecule at a distance of 2.667(5) Å. This carboxyl oxygen originates from an adjacent copper glycinate, in which the O4 of one molecule lies close to the copper of another molecule as shown in the unit cell (figure 2). The chelate angles O2–Cu–N1 and O3–Cu–N2 are smaller than the external angles O2–Cu–O3 and N1–Cu–N2 by approximately 10° but the sum of these angles is 360°

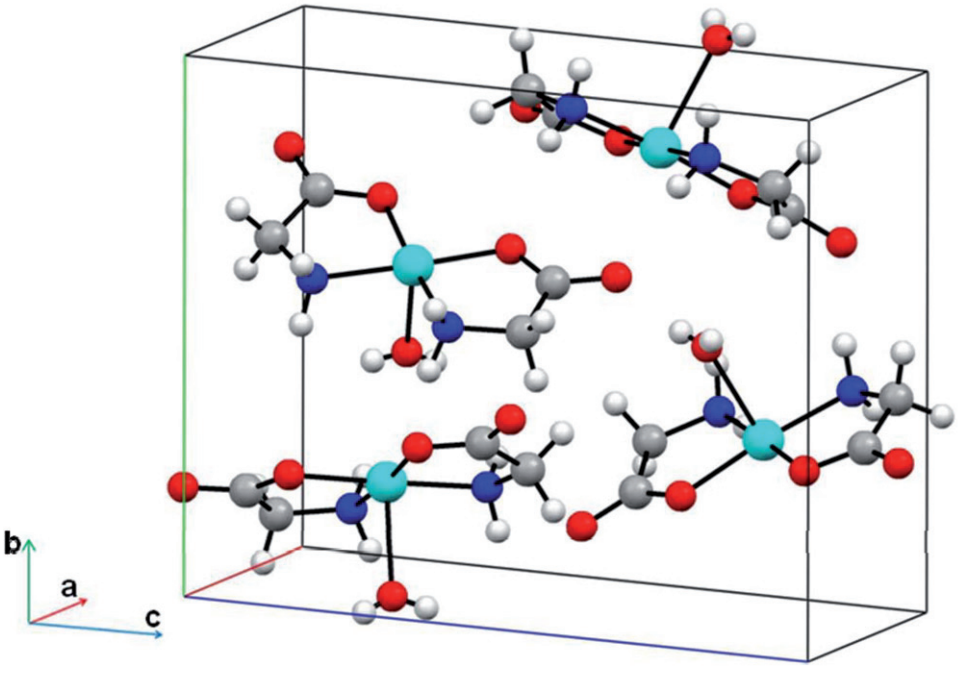

Figure 2. Ball-and-stick representation of the copper glycinate molecules within the unit cell of the compound. Note that O4 of the C3 carboxyl group near the center of the unit cell is near (2.667 Å) the copper ion of the molecule at the top of the cell. The hydrogens, represented as small white spheres, form hydrogen bonds as shown in figure 3 and table S1.

indicating planarity of the rings. Three of the angles forming the square plane to O(1W) are close to 90°, but N2–Cu–O(W1) is 96.10(10)° showing a slight tilt away from N2.

Figure 3 shows an extended unit cell with the hydrogen bonds as dotted lines. Both nitrogens and the water are involved in hydrogen bonds as donors (table S1). The water hydrogens bond to the carboxyl oxygens O1 and O4 in two different molecules. The H-bond donor–acceptor distances are 2.762 Å (O(1W)–H(1WA)···O4) and 2.806 Å (O(1W)–H(1WB)···O1). Only N1–H(1B) hydrogen bonds to O2 at a distance of 3.098 Å. N2; however, hydrogen bonds to O3 through H(2A) at 3.001 Å and to O1 at 2.953 Å through H(2B). Thus, the weak bond between the carbonyl oxygen O4 and Cu and the H_2O and $–NH_2$ hydrogen bonding to the carbonyl oxygens ties the structure into a supramolecular unit.

3.2. *Crystal structure of zinc glycinate, $Zn_4[O_2CCH_2NH_2]_8 \cdot 4H_2O$*

This structure exhibits a measure of disorder which will be described after consideration of the basic structure. There are two unique zincs, each chelated by two glycinates. However, the nitrogens and oxygens are *trans* rather than *cis* as in the copper compound. These individual zinc glycinate groups are connected to each other in the following way. The O6 of Zn2 bonds to Zn1, making it five coordinate as shown in figure 4. In turn, O4 of Zn1 bonds to Zn2 as shown in figure 5. Both these bridging

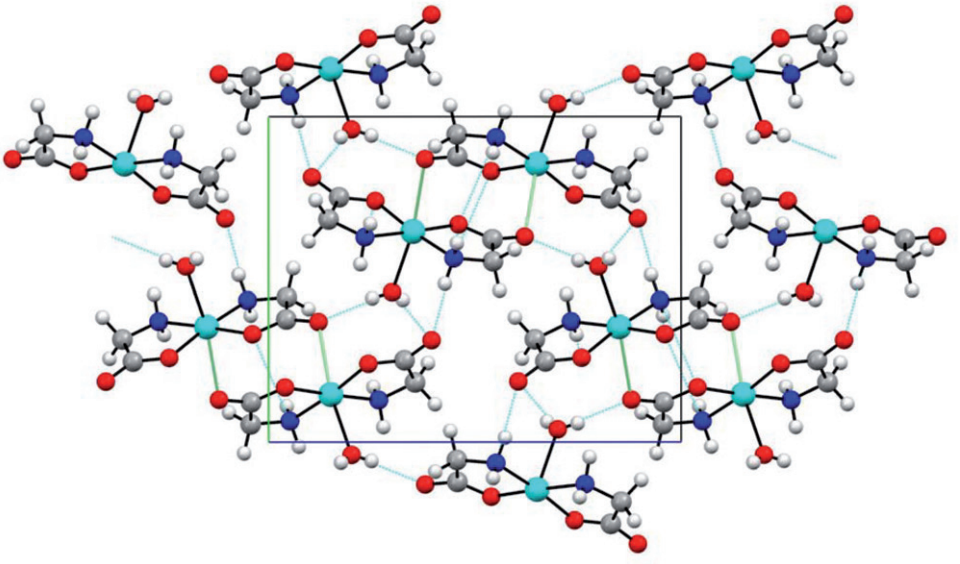

Figure 3. An extended version of the unit cell showing the hydrogen bonds as dotted lines.

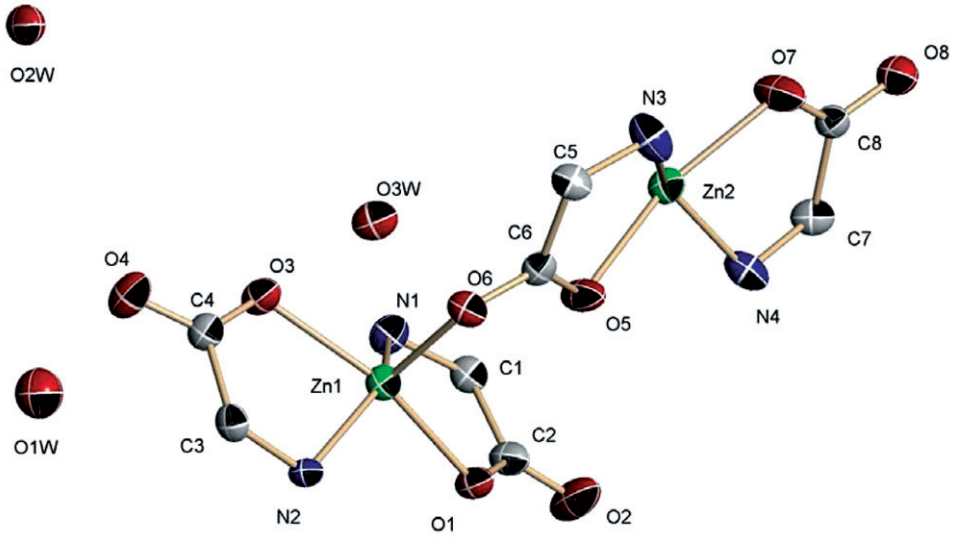

Figure 4. ORTEP representation of the zinc glycinate dimer at the 50% probability level together with the numbering scheme used in the structure solution. The disordered Zinc 3 and the hydrogens are omitted for clarity. The large vibratory motion of O2 and O7 may result from the disorder. Color scheme: Zn(green), remainder as in figure 1.

oxygens are from carboxyl groups. This bonding creates a tetramer in which O2 and O8 are dangling oxygens of carboxyl groups C2 and C8, respectively. There is a center of symmetry in the center of the tetramer so that the bond distances and angles are the same for the second half of the tetramer. The bond distances in the zinc structure are

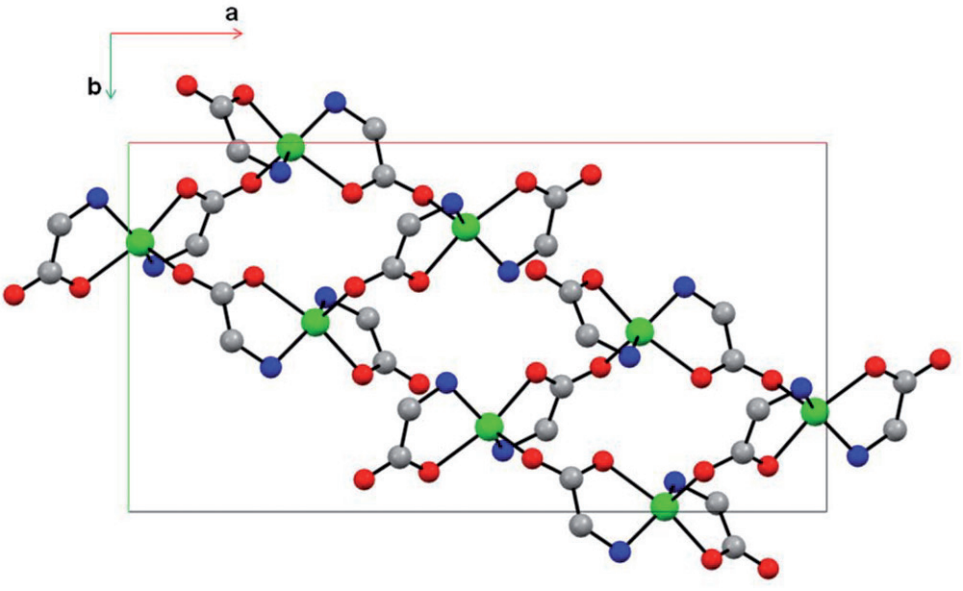

Figure 5. A ball-and-stick representation of two tetramers that propagate along the ab diagonal. There is a similar set of tetramers at 1/2c that runs from the lower end of the unit cell to the upper end, i.e., in the opposite direction of the tetramers pictured.

similar but slightly larger than those for the copper glycinate structure, as expected, since Zn^{2+} is slightly larger than Cu^{2+}. However, there is no regularity to the Zn(3) bond distances where large variations in the Zn–N and Zn–O distances are observed.

The chelate rings are oriented such that the connecting linkage O4 to Zn2 and O6 to Zn1 are almost perpendicular to the rings. For example, if we examine the bond angles between O6 and Zn1 with O1, O3, N_1, and N_2, they are, respectively, 103°, 95°, 111°, and 109° (table 3), all greater than 90° because the two five-membered rings are tilted downward from each other. This is evident by the O3–Zn1–O1 angle, 161.7° and N1–Zn–N2 angle, 138.7°, which significantly deviate from 180°. The bond angles that O4 makes with the Zn2 glycinate chelate rings are similar to those between O6 and Zn1-rings, indicating that the alternating Zn1, Zn2-diglycinate rings are almost perpendicular to each other. Thus, the Zn coordination is best described as a distorted square pyramid.

Unlike the copper glycinate structure the chelate rings are not planar, but are described as butterfly wing shaped. Comparison of the O1–Zn–O3 angle, 161.7(2)°, and N(1)–Zn(1)–N(2) angle, 138.7(2)°, reveals that they are unequal. Furthermore, the O6–Zn1–N and O angles are all greater than 90°. This means that the chelate rings are pushed away from O6. The same is true for O4 and the Zn(2) chelate rings, but in the opposite direction. The butterfly effect is further reinforced when considering the bond angles within the chelate rings. Adding up the angles around Zn1 yields a total of 347.5° rather than 360° as observed for the planar copper glycinate. Thus, the tetramers align along the ab diagonal, as shown in figure 5. There is another such group at 1/2c that runs from the lower left to upper right.

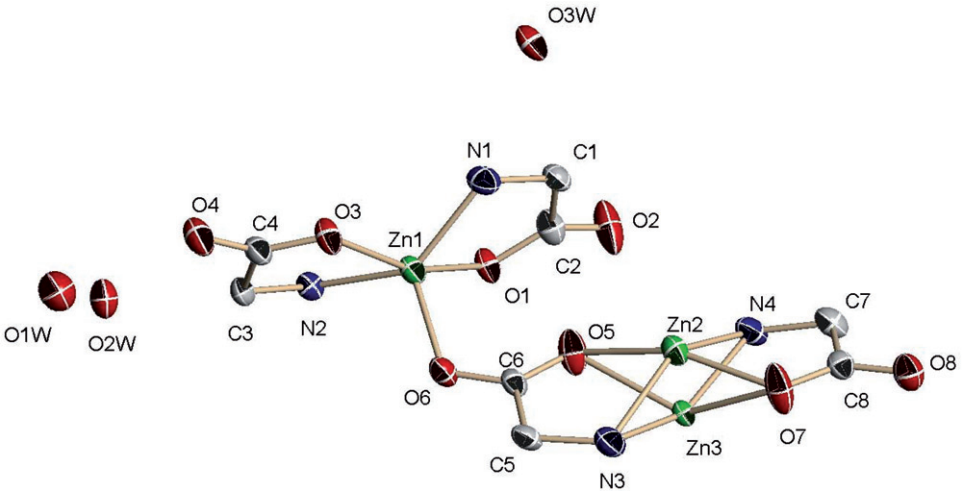

Figure 6. This figure is the same as figure 4 except that Zn3 is included. This positioning of Zn3 inverts the butterfly effect to be concave rather than convex.

We have designated Zn3 to account for the disorder in the crystals. It is the Zn2 that is disordered over two positions; the one we have designated as Zn2 in figure 4 has 75% occupancy and the Zn3 position fills 25% of the occupancy. This position is about 0.89 Å, alternately above and below that of Zn2 in the tetramer, as shown in figure 6. Examination of three separate crystals provided the same end result which may stem from a twinned crystal effect. There are three distinct water molecules in the unit cell; however, two are in special positions, 0*y*¾, 0½¾ and therefore each of these have four rather than eight positions. The remaining water has eight positions providing 16 water molecules in total. Thus, there are four water molecules for each quartet of Zn atoms. These water molecules reside between the rows of tetramers, as shown in figure 7, forming hydrogen bonds with each other and with the zinc glycinate groups to bind the structure in three dimensions as given in table S1 of "Supplementary material."

3.3. *Mass spectrometry*

The electrospray mass spectrographs for the two metal glycinates are shown in figure 8(a) and (b). Both spectra confirm the polymeric nature of the two metal glycinates. In the case of the copper compound, there is a very small peak in the mass range 871, which indicates four copper glycinate units with two of the four water molecules retained (880). The peak at 455 is equivalent to two full copper glycinate units minus two hydrogens, and other units are designated in figure 8(a). The major peaks represent monomers. The polymeric species arise from the closeness of the carboxy oxygen of one unit to the underside of a Cu from an adjacent unit.

In the zinc spectrograph, the highest mass recorded is 640. Because all the water molecules are not bonded to metal atoms, it is expected that they would be removed.

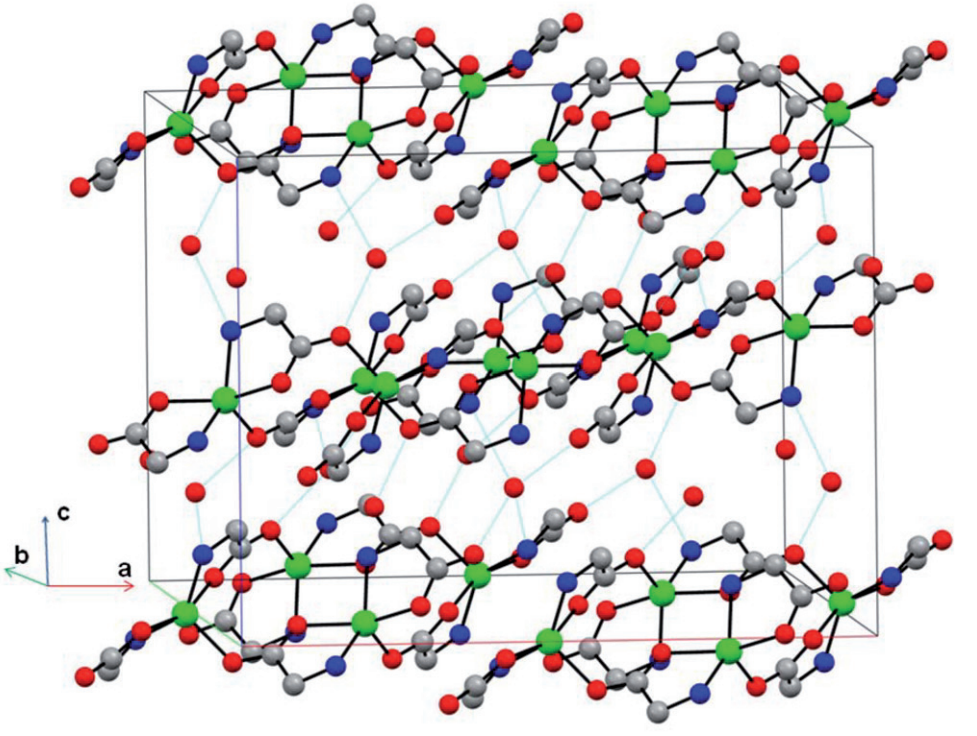

Figure 7. A ball-and-stick representation of the zinc glycinate unit cell showing the positioning of the water molecules. The slotted lines represent hydrogen bonds. The water molecules are all four coordinate acting as donors to the carboxylate oxygens and acceptors from nitrogens.

Thus, the mass of a tetramer zinc glycinate sans water is 854. Three zinc glycinates amount to 640 in agreement with the highest mass peak. Two zinc glycinate units yield a mass of 427 with the masses grouped at 427. Additional mass units are indicated on the spectrogram.

4. Conclusion

This study has shown unequivocally that the glycinatozinc dihydrate is a disordered tetramer. Two chelated ions are bonded to each other by one of the carboxyl oxygens that is not part of the chelate ring forming a dimer. The dimers are in turn bonded to each other by another carboxyl oxygen. Thus, four of the eight carboxyl oxygens bond to zinc producing a somewhat distorted square pyramidal coordination for each zinc. This leaves four uncoordinated carboxyl oxygens that along with the water and $-NH_2$ groups are involved in an intricate array of hydrogen bonds tying the tetramers into a supramolecular array. In about 25% of the molecules, Zn(2) is shifted into the Zn(3) position that also creates a somewhat distorted tetramer.

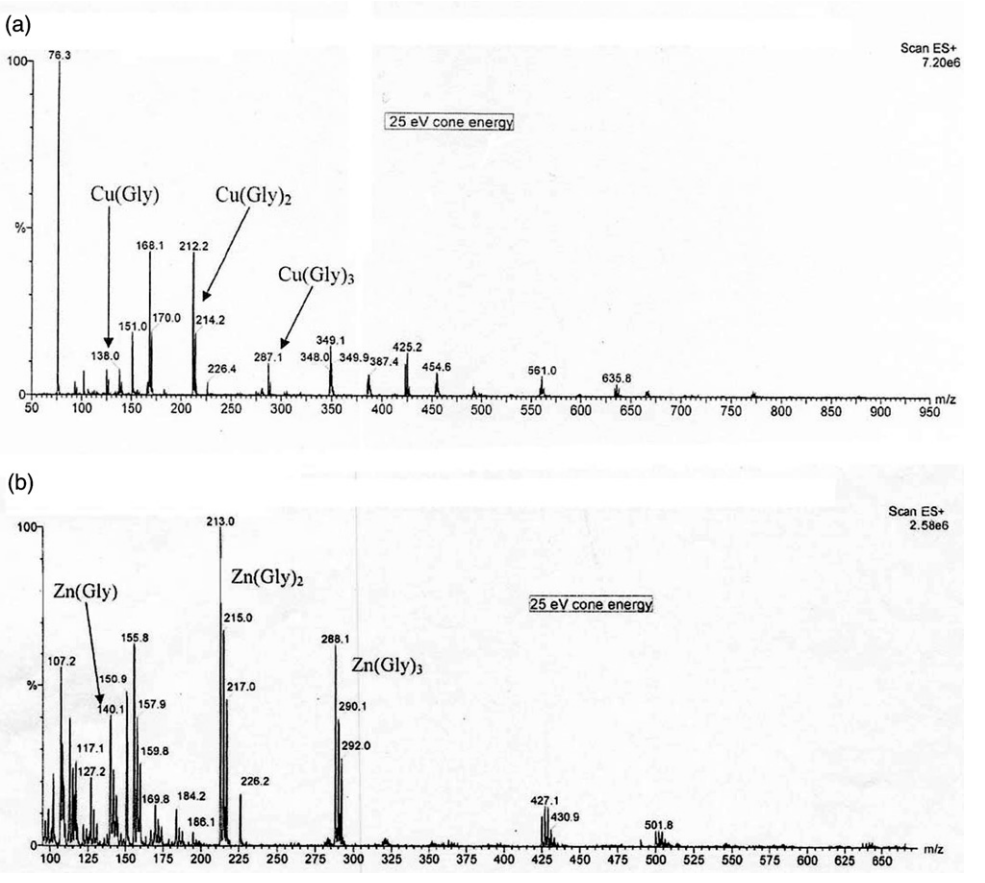

Figure 8. Electrospray mass spectra of copper glycinate (a) and zinc glycinate (b) showing the high molecular weight particles generated.

The copper glycinate is five coordinate with four bonds arising from two glycine molecules chelating Cu(II) through carboxyl oxygen and amino-nitrogen. The fifth coordination site is occupied by water at 0.37 Å longer bond distance than the chelation bonds. The molecules arrange themselves such that free carboxyl oxygen not involved in chelation occupies a position that would be axial to the water creating an octahedral arrangement of the bonding atoms. However, this Cu–O distance of 2.679 Å is outside the range of a normal bond. Nevertheless, it does constitute an electrostatic attraction that together with the hydrogen bonding creates a stable supermolecular array of molecules.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with CCDC reference numbers 787528 and 787529. These data can be obtained

free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336300; E-mail: deposit@ccdc.cam.ac.uk.

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