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Structural and spectral characterization of the compounds $nGly \cdot ZnCl_2 \cdot mH_2O$ (n = 1,2,3; m = 0,2)

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ABSTRACT

The coordination behaviour of Zn^{2+} ions in chloride-glycine aqueous solutions and the formation of different complexes were discussed to predict the crystallization of compounds. The crystal structures of three compounds, Gly-ZnCl₂, 2Gly-ZnCl₂·2H₂O and 3Gly-ZnCl₂, crystallizing from the above solutions were determined. The data showed the building units of the crystal structures of compounds 2Gly-ZnCl₂·2H₂O (monoclinic crystal system, space group C2/c) and 3Gly-ZnCl₂ (orthorhombic crystal system, space group Pna_1) to be discrete distorted electroneutral tetrahedra [Zn(Gly)₂Cl₂], only differing in the position of Cl⁻ ions (*trans* or *cis*), and isolated H₂O molecules or Gly zwitterions. Infinite chains of [Zn(Gly)_{2/2}Cl₂] tetrahedra build the crystal structure of the compound Gly-ZnCl₂ (monoclinic crystal system, space group $P2_1$), thus forming a coordination polymer. The Cl⁻ ions, contrary to the monodentate coordination in the previous two structures. The FTIR and FT Raman spectra of all three compounds were recorded and discussed. Their thermal behaviour was also studied, the similarities and differences were explained by the structura features.

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1. Introduction

Glycin (Gly, α -aminoacetic acid) forms complexes with different inorganic compounds. Some of them, e.g. triglycine sulphate (TGS) [1], triglycine selenate (TGSe) [2], Gly·AgNO₃ [3] and *n*Gly·MeX₂·2H₂O (Me = Mn, Co; X = Cl, Br; *n* = 1,2) [4–6] are known to have ferroelectric properties, or, e.g. 2Gly·MnCl₂·2H₂O [7], a high biological activity. Recently the compound 2Gly·ZnCl₂·2H₂O was proved to have a potential to regulate the activities of antioxidant enzymes as well as essential trace elements during fasciolosis in rats [8,9] and during parasitoses in chicks [10].

The purpose of this paper is to elucidate the coordination behavior of Zn^{2+} in chloride-glycine aqueous solutions and to characterize the crystallizing compounds. Zn^{2+} is a biologically active trace element whose deficiency is likely to affect a number of different enzyme systems. The literature data on zinc-glycine compounds are very limited and concern only the system Gly–ZnCl₂–H₂O [11]. In this paper, crystal structures, vibrational spectra and the results of TG-DTA measurements on three compounds, Gly-ZnCl₂, 2Gly-ZnCl₂.2H₂O and 3Gly-ZnCl₂, crystallizing from the above system, are presented and discussed.

2. Experimental

Three compounds, Gly-ZnCl₂, 2Gly-ZnCl₂·2H₂O and 3Gly-ZnCl₂, were obtained from aqueous solutions of Gly and ZnCl₂ by the method of isothermal evaporation of the solvent. The molar ratios were 1:3, 1:1 and 3:1, respectively. The preparative temperature for the first compound was 50 °C and for the others 25 °C. Analytical reagents were used. The anhydrous compound Gly-ZnCl₂ hydrated easily while the other two compounds, 2Gly·ZnCl₂·2H₂O and 3Gly.ZnCl₂, were stable under standard conditions. The composition of the solid phases was confirmed by chemical analyses. Titrimetric methods (complexometric for Zn²⁺ ions and neutralization analysis in the presence of formaldehyde for Gly [12]) were applied. The accuracy of the analysis was about 0.1-0.2%. The water content in the crystal phases was determined gravimetrically and by TG analysis. The N,O-deuterated compounds were prepared by repeated recrystallization of natural compounds from D₂O (99%) in a desiccator over KOH.

The X-ray data collection was carried out on an Enraf-Nonius CAD4-MACH III four circle diffractometer (MoK α radiation, graphite monochromator). The intensity was corrected for the Lorentzpolarization factor. The positions of non-hydrogen atoms were determined using direct methods (SIR-92) [13], and the hydrogen atoms were localized on differential Fourier maps. The thermal parameters were refined anisotropically for the non-hydrogen

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atoms and isotropically for the hydrogen atoms. Refinement of coordinates and thermal parameters was carried out by the least squares method using the SHELXL 97 program [14]. Crystallographic data for Gly.ZnCl₂, 2Gly.ZnCl₂·2H₂O and 3Gly·ZnCl₂ were deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 685696, CCDC 685697 and CCDC 685698, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CG21, EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

The infrared spectra were recorded by DRIFTS and nujol or fluorolube mull (KBr and AgCl windows) techniques on a Nicolet Magna 760 FTIR spectrometer with 2 cm⁻¹ resolution and Happ-Genzel apodization in the 400–4000 cm⁻¹ region.

The Raman spectra of polycrystalline samples were recorded on a Nicolet Magna 760 FTIR spectrometer equipped with Nicolet Nexus FT Raman module (2 cm⁻¹ resolution, Happ-Genzel apodization, 1064 nm Nd:YVO₄ laser excitation, 300 mW power at the sample) in the 100–3700 cm⁻¹ region.

TG-DTA measurements were carried out on Simultaneous Thermal Analysis Netzsch STA 409, QMG 420. Measurements were done in synthetic air–atmosphere flowing at a rate of 75 ml/min. Analysis range was 20–750 °C, heating rate, 10 °C/min, and Al_2O_3 was the reference. Sample weight was about 50 mg.

3. Results and discussion

The crystallization from solutions is determined by the available complexes which can be incorporated into the crystal structure without being changed. In the zinc chloride-glycine aqueous solutions under consideration Cl^- ions, H_2O molecules and Gly zwitterions compete for being involved in the coordination shell of Zn^{2+} ions, thus forming complexes. The formation of zinc complexes is connected with appropriate Zn^{2+} -ligand bond energies. The coordination of Gly zwitterions occurs easily and may be achieved by means of oxygen atoms from the carboxyl groups (monodentate or bidentate) or a nitrogen atom from the amino groups, or by both simultaneously, the first one being more probable. Due to the low energy of the Zn²⁺-Cl bond and the high energy of the Zn²⁺-H₂O bond, only the participation of Cl⁻ ions in the formation of zinc complexes is probable. Formation of tetrahedral zinc-glycine, zinc-chloride and mixed zinc-chloride-glycine complexes $[Zn(Gly)Cl_3],$ $[Zn(Gly)_2Cl_2]$ and [Zn(Gly)₃Cl] is possible in the saturated solutions, but the mixed complexes are predominating. Depending on the conditions (composition of the solution and temperature) the equilibrium is shifted towards different ratios of these complexes. The complexes [Zn(Gly)₂Cl₂] are of a high stability on account of the geometrical factors. The salt crystallization depends on the sufficiently high thermodynamic activity in the solution of the complexes characteristic of its crystal structure and the stability of this crystal structure.

3.1. Crystal structures

The crystal structures of the compounds $2\text{Gly}\cdot\text{ZnCl}_2\cdot2\text{H}_2\text{O}$ and $3\text{Gly}\cdot\text{ZnCl}_2$ have been found to be analogous. Their building units are discrete distorted electroneutral tetrahedra [Zn(Gly)₂Cl₂] and isolated H₂O molecules (Fig. 1) or Gly zwitterions (Fig. 2). The tetrahedra in both structures differ in the position of Cl⁻ ions only: *trans* for 2Gly·ZnCl₂·2H₂O and *cis* for 3Gly·ZnCl₂. The Gly zwitterions are monodentately coordinated to the Zn²⁺ ion by one oxygen atom from the carboxyl group. The compound 2Gly·ZnCl₂·2H₂O crystallizes in the monoclinic crystal system, space group *C*2/*c* and the compound 3Gly·ZnCl₂ in the orthorhombic crystal system, space group *P*na2₁. All relevant crystallographic data are listed in Table 1.

Infinite chains of $[Zn(Gly)_{2/2}Cl_2]$ tetrahedra build the crystal structure of the Gly-ZnCl₂ compound, thus forming a coordination polymer (Fig. 3). Contrary to the previous two structures, in this compound the glycine zwitterions are bidentately coordinated to two neighbouring Zn²⁺ ions by the two oxygen atoms from their carboxyl groups. The Cl⁻ ions are in *cis*-position, similarly to the



Fig. 1. Crystal structure of 2Gly-ZnCl₂·2H₂O with the atom numbering scheme and anisotropic displacement ellipsoids.



Fig. 2. Crystal structure of 3Gly-ZnCl₂ with the atom numbering scheme and anisotropic displacement ellipsoids.

Table 1

Basic crystallographic data, data collection, and refinement parameters of 2Gly-ZnCl₂-2H₂O, 3Gly-ZnCl₂ and Gly-ZnCl₂

	2Gly·ZnCl ₂ ·2H ₂ O	3Gly·ZnCl ₂	Gly-ZnCl ₂
CCDC No.	685697	685698	685696
Empirical formula	$C_4H_{14}N_2O_6Cl_2Zn$	$C_6H_{15}N_3O_6Cl_2Zn$	C ₂ H ₅ Cl ₂ NO ₂ Zn
Formula weight	322.44	361.48	211.36
Temperature	293(2)K	293(2)K	293(2) K
Wavelength	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, C2/c	Orthorhombic, <i>P</i> na2 ₁	Monoclinic, P2 ₁
Unit cell dimensions	$a = 14.4311(6)$ Å $\alpha = 90^{\circ}$	$a = 15.247(2) \text{ Å} \alpha = 90^{\circ}$	$a = 4.7330(1)$ Å; $\alpha = 90^{\circ}$
	b = 6.9116(3) Å	b = 11.2090(10) Å	b = 10.8650(3) Å;
	$\beta = 126.170(3)^{\circ}$	$\beta = 90^{\circ}$	$\beta = 95.978(2)^{\circ}$
	$c = 14.1803(5) \text{ Å } \gamma = 90^{\circ}$	$c = 15.5530(10) \text{ Å } \gamma = 90^{\circ}$	$c = 6.2050(2)$ Å; $\gamma = 90^{\circ}$
Volume	1141.79(8)Å ³	2658.7(5) Å ³	317.351(15) Å ³
Z, Calculated density	4, 1.876 g/cm ³	8, 1.807 g/cm ³	$2, 2.212 \text{ g/cm}^3$
Absorption coefficient	2.629 mm^{-1}	2.272 mm^{-1}	4.617 mm^{-1}
F(000)	656	1472	208
Crystal size	$0.3\times0.3\times0.2\ mm$	$0.2 \times 0.3 \times 0.4 \text{ mm}$	0.5 imes 0.4 imes 0.4 mm
θ Range for data collection	3.19–24.97°	2.24–24.97°	3.75–27.50°
Index ranges	h(-17;13), k(0;8), l(-11;16)	h(0;18), k(0;13), l(0;18)	h(-6;5), k(-14;13), l(-8;8)
Reflections collected/ unique	1357/1005 [<i>R</i> (int) = 0.0662]	2428/2428	4808/1429 [<i>R</i> (int) = 0.0661]
Completeness to θ	$\theta = 24.97^{\circ} \ 93.7\%$	$\theta = 24.97^{\circ} \ 90.9\%$	$\theta = 27.50^{\circ} \ 99.6\%$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	1005/0/98	2428/0/446	1429/1/94
Goodness-of-fit on F ²	1.158	1.071	1.071
Final R indices	$R_1 = 0.0286, wR_2 = 0.0668$	$R_1 = 0.0218, wR_2 = 0.0549$	$R_1 = 0.0356, wR_2 = 0.0906$
Reflections observed	986	2222	1426
R indices (all data)	$R_1 = 0.0290, wR_2 = 0.0670$	$R_1 = 0.0276, wR_2 = 0.0577$	$R_1 = 0.0356, wR_2 = 0.0906$
Largest diff. peak and hole	0.580 and -0.807	0.792 and -0.243	0.551 and -0.712
Weighting scheme	$w = [\sigma^2(F_0^2) + (0.0438P)^2 + 0.6101P]^{-1}$ P = [F_0^2 + 2F_c^2]/3	$w = [\sigma^2(F_0{}^2) + (0.0377P)^2 + 0.8087P]^{-1} P = [F_0{}^2 + 2F_c{}^2]/3$	$w = [\sigma^2(F_0^2) + (0.0586P)^2 + 0.2685P]^{-1} P = [F_0^2 + 2F_c^2]/3$

compound 3Gly-ZnCl_{2.} The compound crystallizes in monoclinic crystal system, space group $P2_1$ (Table 1).

The bond distances and angles for the three structures are given in Table 2. They are not significantly different.

The hydrogen bond network for the compound $Gly \cdot ZnCl_2$ is limited only to the bonds of N-H…Cl type connecting different chains (Table 3). Week hydrogen bonds of O-H···O, N-H···O and N-H···Cl type are typical for 2Gly·ZnCl₂·2H₂O (Table 3). Finally, hydrogen bonds of N-H···O and N-H···Cl type are present in 3Gly·ZnCl₂ crystal structure (Table 3).

According to Pauling [15], the least stable of the three structures is that of Gly-ZnCl₂ (third Pauling rule). On this basis we assumed



Fig. 3. Crystal structure of Gly-ZnCl₂ with the atom numbering scheme and anisotropic displacement ellipsoids.

Table 2 Selected bond lengths (Å) and angles (°)

	3Gly-ZnCl ₂ (mol. 1)	3Gly. ZnCl ₂ (mol. 2)	2Gly-ZnCl ₂ .2H ₂ O (instead O(3) read O(1a), instead Cl(2) read Cl(1a))	Gly ZnCl ₂ (in	stead O(3) read O(2))
Geometry of coord	linated shell of Zn ²⁺				
Zn-O(1)	1.967(3)	1.979(3)	1.981(1)	1.982(3)	
Zn-O(3)	1.999(3)	2.013(3)	1.981(1)	1.991(3)	
Zn-Cl(1)	2.238(1)	2.225(2)	2.2346(5)	2.238(1)	
Zn-Cl(2)	2.274(1)	2.267(1)	2.2346(5)	2.246(1)	
O(1) - Zn - O(3)	102.7(1)	103.5(1)	97.84(9)	101.89(13)	
O(1)-Zn-Cl(1)	119.3(1)	121.2(1)	118.80(5)	118.98(10)	
O(1)-Zn- $Cl(2)$	112.4(1)	109.8(1)	107.62(4)	112.79(10)	
O(3)-Zn-Cl(1)	111.3(1)	110.1(1)	118.80(5)	106.18(12)	
O(3)-Zn-Cl(2)	101.5(1)	101.6(1)	107.62(4)	105.88(12)	
Cl(1)-Zn-Cl(2)	108.19(5)	108.82(6)	106.70(3)	109.77(4)	
	3 Gly \cdot ZnCl ₂ (mol. 1)	3Gly·ZnCl ₂ (mol. 2)	2Gly·ZnCl ₂ .2H ₂ O	$Gly \cdot ZnCl_2$	
Coordinated molec	cules Gly				
Zn-O(2)-C(1)	-	-	-	137.65(26)	
Zn-O(1)-C(1)	112.2(3)	112.7(3)	120.6(1)	115.98(28)	
C(1) - O(1)	1.286(5)	1.269(5)	1.265(3)	1.259(5)	
C(1) - O(2)	1.222(6)	1.225(5)	1.240(3)	1.242(5)	
C(1) - C(2)	1.497(7)	1.506(7)	1.513(3)	1.507(5)	
C(2) - N(1)	1.491(7)	1.466(7)	1.471(3)	1.464(7)	
O(1)-C(1)-O(2)	124.9(4)	125.4(4)	126.4(2)	123.58(36)	
			3Gly·ZnCl ₂ (mol. 8)		3Gly·ZnCl ₂ (mol. 9)
Non-coordinated r	nolecule Gly (for 3Gly Z	nCl_2 only)			
C(1) - O(1)			1.262(6)		1.263(6)
C(1) - O(2)			1.256(6)		1.245(6)
C(1) - C(2)			1.506(8)		1.524(8)
C(2) - N(1)			1.472(6)		1.478(7)
O(1)-C(1)-O(2)			125.0(6)		127.1(5)
			3Gly·ZnCl ₂ (mol. 1)		3Gly·ZnCl ₂ (mol. 2)
Coordinated molec	cule Gly (for 3Gly ZnCl ₂	only)			
Zn-O(3)-C(3)			113.0(3)		115.1(3)
C(3) - O(3)			1.278 (6)		1.276(5)
C(3) - O(4)			1.222(6)		1.236(6)
C(3) - C(4)			1.512(7)		1.520(6)
O(4)-N(2)			1.457(7)		1.466(6)
O(3)-C(3)-O(4)			125.8(4)		125.6(4)

and proved the compound Gly·ZnCl₂ to crystallize at high temperatures (50 °C). The compounds 2Gly·ZnCl₂·2H₂O and 3Gly·ZnCl₂ have to crystallize easily even at low temperatures. Contrary to Balkunova et al. [11], we have proved the existence of the compound 3Gly·ZnCl₂ even at 25 °C.

3.2. Vibrational spectra

The FTIR and FT Raman spectra of Gly·ZnCl₂, 2Gly·ZnCl₂·2H₂O and 3Gly·ZnCl₂ recorded at room temperature are depicted in Figs. 4–6,

respectively. The assignment of the observed bands (Tables 4–6) is based on recent papers [16,17] concerning vibrational spectra of glycine and our previous paper [18] focused on glycine adducts. The assignment of deformation vibrations of the NH_3^+ group was confirmed by recording and analysis of spectra of N,O-deuterated analogues. Vibrational manifestations connected with formation of tetrahedral Zn^{2+} complexes (i.e. vZn–Cl and vZn–O vibrations) were assigned according to papers [19,20] dealing with zinc complexes. And finally, assignment of the bands corresponding to the O–H and N–H stretching vibrations are in agreement with the curves

Table	3
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Hydrogen bonds in the compounds 2Gly-ZnCl₂·2H₂O, 3Gly-ZnCl₂ and Gly-ZnCl₂

Hydrogen bonds with HA < r(A) + 2.000 Å and <dha> 110'$ZGV_2GV_2, 2H_2O'$$ZGV_2GV_2, 2H_2O'$N1-H110.82(4)2.66(3)124(4)3.180(3)CI [x1/2, y+1/2, -2]N1-H120.80(3)2.10(3)166(3)2.887(3)0.9 [x, -y+1, 2+1/2]0.9 H910.85(4)2.01(4)176(3)2.876(3)0.9 [x, -y+1, 2+1/2]0.9 -H920.70(5)2.22(5)173(4)2.918(3)0.2 [-x, -y+1, -z]2GV_2GC_2N1-H110.84(5)1.99(5)166(5)2.966(6)0.92 [x, y-1, 2]N11-H1130.76(5)2.22(5)155(4)2.891(6)0.81 [-x-1/2, y-1/2, 2]N12-H1210.82(5)2.13(5)155(4)2.891(6)0.81 [-x-1/2, y-1/2, 2]N12-H1230.94(7)2.17(6)135(5)2.915(6)0.91 [x-1/2, -y-1/2, 2]N12-H1230.94(7)2.67(8)176(6)3.464(5)C122 [x-1/2, -y-1/2, 2]N12-H1230.94(7)2.61(8)116(5)3.166(5)C121 [x-1/2, -y-1/2, 2]N12-H2141.32(6)1.51(6)154(5)2.755(6)0.92 [x, y-1, 2]N21-H2150.776(6)2.23(7)170(5)2.978(6)0.92 [x, y-1, 2]N21-H2140.96(9)1.77(9)167(6)3.926(6)0.94 [x, y-1, 2]N21-H2150.76(6)2.23(7)170(5)2.978(6)0.92 [x, y-1, 2]N21-H2140.77(6)2.51(6)156(5)3.233(6)0.14 [x, y+1, 2]N21-H2150.776(6)2.78(5)122(6)3.64(5</dha>	D-H	d(D-H)	<i>d</i> (H…A)	<dha< th=""><th><i>d</i>(D…A)</th><th>А</th></dha<>	<i>d</i> (D…A)	А
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Hydrogen bonds witl 2Gly·ZnCl ₂ ·2H ₂ O	h H…A < r(A) + 2.000 Å and <	<dha>110°</dha>			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-H11	0.82(4)	2.46(3)	145(4)	3.174(3)	O2[-x-1/2, -y+1/2, -z]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-H11	0.82(4)	2.65(3)	124(4)	3.180(3)	Cl $[x-1/2, y+1/2, z]$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-H12	0.80(3)	2.10(3)	166(3)	2.887(3)	09[-x-1/2, -y+3/2, -z]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N1-H13	0.87(4)	2.01(4)	176(3)	2.876(3)	09 $[x, -y+1, z+1/2]$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O9-H91	0.85(4)	2.05(4)	171(5)	2.884(3)	02
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O9-H92	0.70(5)	2.22(5)	173(4)	2.918(3)	O2 $[-x, -y+1, -z]$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3Gly-ZnCl ₂					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N11-H111	0.84(5)	1.99(5)	160(5)	2.796(6)	O92 $[x, y-1, z]$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N11-H113	0.76(5)	2.22(5)	165(5)	2.965(6)	013 $[x+1/2, -y-1/2, z]$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N12-H121	0.82(5)	2.13(5)	155(4)	2.891(6)	$081 \left[-x - 1/2, y - 1/2, z + 1/2 \right]$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N12-H122	0.79(8)	2.67(8)	176(6)	3.464(5)	Cl22 $[x-1/2, -y-1/2, z]$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N12-H123	0.94(7)	2.17(6)	135(5)	2.915(6)	091 [x-1/2, -y-1/2, z]
N21-H2111.32(6)1.51(6)154(5)2.755(6)O82 [x, y+1, z]N21-H2120.76(6)2.23(7)170(5)2.978(6)O23 [x-1/2, -y+1/2, z]N21-H2130.77(6)2.51(6)156(5)3.233(6)O14 [x, y+1, z]N21-H2130.77(6)2.78(5)122(6)3.264(5)C111 [x, y+1, z]N22-H2211.05(9)1.77(9)167(6)2.796(6)O92 [-x+1, -y+1, 2, -1/2]N22-H2220.78(8)2.26(8)167(6)3.032(6)O81 [x+1/2, -y+1/2, z]N81-H8110.76(6)2.12(6)149(5)2.797(6)O12 [x-1/2, -y-1/2, z]N81-H8121.04(7)1.75(8)168(5)2.782(6)O91 [-x, -y, z-1/2]N81-H8130.76(6)2.19(5)161(5)2.923(6)O24 [x-1/2, -y+1/2, z]N91-H9110.88(6)2.07(6)138(5)2.781(6)O22 [x+1/2, -y+1/2, z]N91-H9121.02(6)1.96(7)152(8)2.898(5)O14 [x+1/2, -y+1/2, z]N91-H9130.87(5)1.90(5)174(4)2.767(5)O82 [-x+1/2, y+1/2, z]Cly.ZnCl2UUUUUUUN1-H1A0.89(9)2.79(9)141(7)3.532(6)C11 [x, y, z-1]N1-H1B0.97(10)2.43(10)140(8)3.232(5)C12 [-x+1, y+1/2, -z]	N12-H123	0.94(7)	2.64(8)	116(5)	3.166(5)	Cl21 $[x-1/2, -y-1/2, z]$
N21-H2120.76(6)2.23(7)170(5)2.978(6)O23 $[x-1/2, -y+1/2, z]$ N21-H2130.77(6)2.51(6)156(5)3.233(6)O14 $[x, y+1, z]$ N21-H2130.77(6)2.78(5)122(6)3.264(5)C111 $[x, y+1, z]$ N22-H211.05(9)1.77(9)167(6)2.796(6)O92 $[-x+1, -y+1, z-1/2]$ N22-H220.78(8)2.26(8)167(6)3.032(6)O81 $[x+1/2, -y+1/2, z]$ N81-H8110.76(6)2.12(6)149(5)2.797(6)O12 $[x-1/2, -y-1/2, z]$ N81-H8121.04(7)1.75(8)168(5)2.782(6)O91 $[-x, -y, z-1/2]$ N81-H8130.76(6)2.19(5)161(5)2.923(6)O24 $[x-1/2, -y+1/2, z]$ N91-H9110.88(6)2.07(6)138(5)2.781(6)O22 $[x+1/2, -y+1/2, z]$ N91-H9110.88(6)2.72(6)131(5)3.361(3)C121 $[x+1/2, -y+1/2, z]$ N91-H9121.02(6)1.96(7)152(8)2.898(5)O14 $[x+1/2, -y-1/2, z]$ N91-H9130.87(5)1.90(5)174(4)2.767(5)082 $[-x+1/2, y+1/2, -z]$ Cly-ZnCl2VVV1.31(7)3.215(5)C12 $[-x, y+1/2, -z]$ N1-H1A0.89(9)2.79(9)141(7)3.532(6)C11 $[x, y, z-1]$ N1-H1B0.97(10)2.43(10)140(8)3.232(5)C12 $[-x+1, y+1/2, -z]$	N21-H211	1.32(6)	1.51(6)	154(5)	2.755(6)	O82 [x, y+1, z]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N21-H212	0.76(6)	2.23(7)	170(5)	2.978(6)	O23 $[x-1/2, -y+1/2, z]$
N21-H2130.77(6)2.78(5)122(6)3.264(5)Cl11 [x, y+1, z]N22-H2211.05(9)1.77(9)167(6)2.796(6)092 [$-x+1$, $-y+1$, $z-1/2$]N22-H2220.78(8)2.26(8)167(6)3.032(6)081 [$x+1/2$, $-y+1/2$, z]N81-H8110.76(6)2.12(6)149(5)2.797(6)012 [$x-1/2$, $-y-1/2$, z]N81-H8121.04(7)1.75(8)168(5)2.782(6)091 [$-x$, $-y, z-1/2$]N81-H8130.76(6)2.19(5)161(5)2.923(6)024 [$x-1/2$, $-y+1/2$, z]N91-H9110.88(6)2.07(6)138(5)2.781(6)022 [$x+1/2$, $-y+1/2$, z]N91-H9110.88(6)2.72(6)131(5)3.361(3)Cl21 [$x+1/2$, $-y+1/2$, z]N91-H9121.02(6)1.96(7)152(8)2.898(5)014 [$x+1/2$, $-y-1/2$, z]N91-H9130.87(5)1.90(5)174(4)2.767(5)082 [$-x+1/2$, $y+1/2$, $z+1/2$] <i>Gly.ZnCl₂NNN</i> 1.41(7)3.532(6)Cl1 [x , y , $z-1$]N1-H1A0.89(9)2.79(9)141(7)3.532(6)Cl1 [x , y , $z-1$]N1-H1B0.97(10)2.43(10)140(8)3.232(5)Cl2 [$-x+1$, $y+1/2$, $-z$]	N21-H213	0.77(6)	2.51(6)	156(5)	3.233(6)	O14 [x, y+1, z]
N22-H2211.05(9)1.77(9)167(6)2.796(6)O92 $[-x+1, -y+1, z-1/2]$ N22-H2220.78(8)2.26(8)167(6)3.032(6)O81 $[x+1/2, -y+1/2, z]$ N81-H8110.76(6)2.12(6)149(5)2.797(6)O12 $[x-1/2, -y-1/2, z]$ N81-H8121.04(7)1.75(8)168(5)2.782(6)O91 $[-x, -y, z-1/2]$ N81-H8130.76(6)2.19(5)161(5)2.923(6)O24 $[x-1/2, -y+1/2, z]$ N91-H9110.88(6)2.07(6)138(5)2.781(6)O22 $[x+1/2, -y+1/2, z]$ N91-H9110.88(6)2.72(6)131(5)3.361(3)C12 $[x+1/2, -y+1/2, z]$ N91-H9121.02(6)1.96(7)152(8)2.898(5)O14 $[x+1/2, -y-1/2, z]$ N91-H9130.87(5)1.90(5)174(4)2.767(5)O82 $[-x+1/2, y+1/2, z+1/2]$ <i>GlyZnCl₂N</i> 1-H1A0.89(9)2.56(9)131(7)3.215(5)C12 $[-x, y+1/2, -z]$ N1-H1A0.97(10)2.43(10)140(8)3.232(5)C12 $[-x+1, y+1/2, -z]$	N21-H213	0.77(6)	2.78(5)	122(6)	3.264(5)	Cl11 [x, y+1, z]
N22-H2220.78(8)2.26(8)167(6)3.032(6)081 [x+1/2, -y+1/2, z]N81-H8110.76(6)2.12(6)149(5)2.797(6)012 [x-1/2, -y-1/2, z]N81-H8121.04(7)1.75(8)168(5)2.782(6)091 [$-x, -y, z-1/2$]N81-H8130.76(6)2.19(5)161(5)2.923(6)024 [x-1/2, -y+1/2, z]N91-H9110.88(6)2.07(6)138(5)2.781(6)022 [x+1/2, -y+1/2, z]N91-H9110.88(6)2.72(6)131(5)3.61(3)Cl21 [x+1/2, -y+1/2, z]N91-H9121.02(6)1.96(7)152(8)2.898(5)014 [x+1/2, -y-1/2, z]N91-H9130.87(5)1.90(5)174(4)2.767(5)082 [$-x+1/2, y+1/2, z$]ClyZnCl2VVVVVVN1-H1A0.89(9)2.56(9)131(7)3.215(5)Cl2 [$-x, y+1/2, -z$]N1-H1B0.97(10)2.43(10)140(8)3.232(5)Cl2 [$-x+1, y+1/2, -z$]	N22-H221	1.05(9)	1.77(9)	167(6)	2.796(6)	O92 [-x+1, -y+1, z-1/2]
N81-H8110.76(6)2.12(6)149(5)2.797(6)O12 $[x-1/2, -y-1/2, z]$ N81-H8121.04(7)1.75(8)168(5)2.782(6)O91 $[-x, -y, z-1/2]$ N81-H8130.76(6)2.19(5)161(5)2.923(6)O24 $[x-1/2, -y+1/2, z]$ N91-H9110.88(6)2.07(6)138(5)2.781(6)O22 $[x+1/2, -y+1/2, z]$ N91-H9110.88(6)2.72(6)131(5)3.361(3)Cl21 $[x+1/2, -y+1/2, z]$ N91-H9121.02(6)1.96(7)152(8)2.898(5)O14 $[x-1/2, -y+1/2, z]$ N91-H9130.87(5)1.90(5)174(4)2.767(5)O82 $[-x+1/2, y+1/2, z+1/2]$ Cly-ZnCl2VVVVVN1-H1A0.89(9)2.56(9)131(7)3.215(5)Cl2 $[-x, y+1/2, -z]$ N1-H1A0.89(9)2.79(9)141(7)3.532(6)Cl1 $[x, y, z-1]$ N1-H1B0.97(10)2.43(10)140(8)3.232(5)Cl2 $[-x+1, y+1/2, -z]$	N22-H222	0.78(8)	2.26(8)	167(6)	3.032(6)	O81 [<i>x</i> +1/2, − <i>y</i> +1/2, <i>z</i>]
N81-H8121.04(7)1.75(8)168(5)2.782(6) $O91 [-x, -y, z-1/2]$ N81-H8130.76(6)2.19(5)161(5)2.923(6) $O24 [x-1/2, -y+1/2, z]$ N91-H9110.88(6)2.07(6)138(5)2.781(6) $O22 [x+1/2, -y+1/2, z]$ N91-H9110.88(6)2.72(6)131(5)3.361(3) $C121 [x+1/2, -y+1/2, z]$ N91-H9121.02(6)1.96(7)152(8)2.898(5) $O14 [x+1/2, -y-1/2, z]$ N91-H9130.87(5)1.90(5)174(4)2.767(5) $O82 [-x+1/2, y+1/2, z+1/2]$ Cly-ZnCl_2VVVVVN1-H1A0.89(9)2.56(9)131(7)3.215(5) $C12 [-x, y+1/2, -z]$ N1-H1A0.89(9)2.79(9)141(7)3.532(6) $C11 [x, y, z-1]$ N1-H1B0.97(10)2.43(10)140(8)3.232(5) $C12 [-x+1, y+1/2, -z]$	N81-H811	0.76(6)	2.12(6)	149(5)	2.797(6)	012 $[x-1/2, -y-1/2, z]$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N81-H812	1.04(7)	1.75(8)	168(5)	2.782(6)	O91 [− <i>x</i> , − <i>y</i> , <i>z</i> −1/2]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	N81-H813	0.76(6)	2.19(5)	161(5)	2.923(6)	O24 $[x-1/2, -y+1/2, z]$
N91-H911 0.88(6) 2.72(6) 131(5) 3.361(3) Cl21 [x+1/2, -y+1/2, z] N91-H912 1.02(6) 1.96(7) 152(8) 2.898(5) 014 [x+1/2, -y-1/2, z] N91-H913 0.87(5) 1.90(5) 174(4) 2.767(5) 082 [-x+1/2, y+1/2, z+1/2] Gly.ZnCl_2 3.215(5) Cl2 [-x, y+1/2, -z] N1-H1A 0.89(9) 2.56(9) 131(7) 3.215(5) Cl2 [-x, y+1/2, -z] N1-H1A 0.89(9) 2.79(9) 141(7) 3.532(6) Cl1 [x, y, z-1] N1-H1B 0.97(10) 2.43(10) 140(8) 3.232(5) Cl2 [-x+1, y+1/2, -z]	N91-H911	0.88(6)	2.07(6)	138(5)	2.781(6)	O22 $[x+1/2, -y+1/2, z]$
N91-H912 1.02(6) 1.96(7) 152(8) 2.898(5) O14 [x+1/2, -y-1/2, z] N91-H913 0.87(5) 1.90(5) 174(4) 2.767(5) O82 [-x+1/2, y+1/2, z+1/2] Gly-ZnCl_2 <	N91-H911	0.88(6)	2.72(6)	131(5)	3.361(3)	Cl21 $[x+1/2, -y+1/2, z]$
N91-H913 0.87(5) 1.90(5) 174(4) 2.767(5) O82 [-x+1/2, y+1/2, z+1/2] Gly-ZnCl_2 N1-H1A 0.89(9) 2.56(9) 131(7) 3.215(5) Cl2 [-x, y+1/2, -z] N1-H1A 0.89(9) 2.79(9) 141(7) 3.532(6) Cl1 [x, y, z-1] N1-H1B 0.97(10) 2.43(10) 140(8) 3.232(5) Cl2 [-x+1, y+1/2, -z]	N91-H912	1.02(6)	1.96(7)	152(8)	2.898(5)	O14 $[x+1/2, -y-1/2, z]$
Gly.ZnCl2 Science Science	N91-H913	0.87(5)	1.90(5)	174(4)	2.767(5)	O82 [- <i>x</i> +1/2, <i>y</i> +1/2, <i>z</i> +1/2]
N1-H1A 0.89(9) 2.56(9) 131(7) 3.215(5) Cl2 [-x, y+1/2, -z] N1-H1A 0.89(9) 2.79(9) 141(7) 3.532(6) Cl1 [x, y, z-1] N1-H1B 0.97(10) 2.43(10) 140(8) 3.232(5) Cl2 [-x+1, y+1/2, -z]	Gly-ZnCl ₂					
N1-H1A 0.89(9) 2.79(9) 141(7) 3.532(6) Cl1 [x, y, z-1] N1-H1B 0.97(10) 2.43(10) 140(8) 3.232(5) Cl2 [-x+1, y+1/2, -z]	N1-H1A	0.89(9)	2.56(9)	131(7)	3.215(5)	Cl2 $[-x, y+1/2, -z]$
N1-H1B 0.97(10) 2.43(10) 140(8) 3.232(5) Cl2 [-x+1, y+1/2, -z]	N1-H1A	0.89(9)	2.79(9)	141(7)	3.532(6)	Cl1 $[x, y, z-1]$
	N1-H1B	0.97(10)	2.43(10)	140(8)	3.232(5)	Cl2 $[-x+1, y+1/2, -z]$



Fig. 4. FTIR (compiled from nujol and fluorolube mulls) and FT Raman spectra of Gly-ZnCl₂.

[21,22] correlating the position of vibrational bands with the length of the appropriate hydrogen bonds found in the crystal structure.

As it was expected, the overall character of the spectra of all three compounds is generally similar. The main differences can be observed in N–H or O–H groups stretching region due to different hydrogen bonding schemes (see Table 3). For the IR spectra of 2Gly-ZnCl₂·2H₂O and 3Gly-ZnCl₂ is also typical the presence of several bands in 1900–2700 cm⁻¹ region, which are characteristic for overtones and combination vibrations.

Unequal coordination of glycine zwitterions in studied crystal structures is reflected in changes of positions of COO⁻ stretching vibrations bands. In the case of Gly·ZnCl₂ (bidentate coordination of glycine) distance between the bands of symmetric and antisymmetric stretching vibrations is much higher compared to spectra of 2Gly·ZnCl₂·2H₂O and 3Gly·ZnCl₂ (monodentate coordination of glycine).

The changes in positions and intensities of bands in the IR spectra corresponding to NH₃⁺ deformation vibrations (which are sensitive



Fig. 5. FTIR (compiled from nujol and fluorolube mulls) and FT Raman spectra of 2Gly-ZnCl₂·2H₂O.



Fig. 6. FTIR (compiled from nujol and fluorolube mulls) and FT Raman spectra of 3Gly-ZnCl₂.

to deuteration) in the 1480–1600 cm⁻¹ region can be correlated with different hydrogen bonding in crystals of all three compounds.

Generally, we can conclude that recorded vibrational spectra of studied compounds are fully in accord with their refined crystal structures. The minor differences in position and splitting of glycine vibrational bands can be also explained by increasing number of structurally independent glycine zwitterions in asymmetric units of Gly·ZnCl₂, 2Gly·ZnCl₂·2H₂O and 3Gly·ZnCl₂, respectively.

3.3. Thermal behaviour

The thermal behaviour of the compounds Gly·ZnCl₂, 2Gly·ZnCl₂·2H₂O and 3Gly·ZnCl₂ shows a significant similarity (Table 7 and [11]) which follows from their crystal structures.

The decomposition scheme only of the crystal hydrate $2Gly \cdot ZnCl_2 \cdot 2H_2O$ slightly differs from those of the anhydrous compounds. Two-steps dehydration was registered – the first step with a temperature maximum at 104 °C when 3/2 molecules of the crystal water eliminate and the second one at 138 °C when $\frac{1}{2}$ molecules of the crystal water eliminate, respectively.

The second thermal process for 2Gly.ZnCl₂.2H₂O and the first one for the anhydrous compounds Gly·ZnCl₂ and 3Gly·ZnCl₂ is the glycine melting which runs together with compounds decomposition. The highest melting temperature (229 °C) was registered for Gly·ZnCl₂, in whose structure more stable bidentate coordination of glycine zwitterions to Zn^{2+} exists. For 3Gly·ZnCl₂ and 2Gly·ZnCl₂·2H₂O with a monodentate coordination of glycine in their structures the melting temperatures are practically equal –

Table 4		
FTIR and FT Raman	spectra of Gly-Zr	ıCl ₂

FT Raman (cm ⁻¹)	FTIR (cm^{-1})	Assignment	FT Raman (cm ⁻¹)	FTIR (cm ⁻¹)	Assignment
154s		Lattice modes		1452s	$\delta_{s} \text{ NH}_{3}^{+}$
165s		ρ CCN	1454m	1460sh	δCH_2
210m		Lattice modes	1471sh	1470sh	
259m			1481s	1478s	$\delta_{\rm s} {\rm NH_3}^+$
302vs		v Zn–Cl	1563m	1563s	$\delta_{as} \text{NH}_3^+$
390m		ρ CCN	1580w	1589s	
511s	511m	$\rho \text{ COO}^-$	1599w	1600s	vas COO ⁻
	558w	v Zn–O		1642s	
587w	587m	ω COO-		1736w	?
	620wb	$\gamma \text{ N-H}(\cdots \text{X})$		2541w	
	682m	$\delta \text{ COO}^-$	2686w	2685w	
708w	709m		2799w		
886w	885m	v _s CCN	2901w	2901m	
	901m	$\rho \text{ CH}_2$		2936m	
919s	919m		2973s	2976m	vs CH2
1031s	1031m	v _{as} CCN	3014m	3012m	vas CH2
1086m	1087m	$\rho \text{ NH}_3^+$		3023m	
1101m	1101w		3098w	3100sh	v N-H(X)
1308s	1309s	ωCH_2	3130w	3133s	
1348s	1348s	τ CH ₂	3190w	3187s	
1412s	1410s	v _s COO ⁻	3235w	3230sh	
	1441s	$\delta \operatorname{CH}_2$		3489m	

Note. Abbreviations and symbols: vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder; v, stretching; δ , deformation or in-plane bending; γ , out-of-plane bending; ρ , rocking; ω , wagging; τ , twisting; s, symmetric; as, antisymmetric; atom X = 0, Cl.

Table 5

FTIR and FT Raman spectra of 2Gly·ZnCl₂.2H₂O

FT Raman (cm ⁻¹)	FTIR (cm^{-1})	Assignment	FT Raman (cm ⁻¹)	FTIR (cm ⁻¹)	Assignment
130m		Lattice modes		1636s	v_{as} COO ⁻
160s		ρ CCN		1653sh	δ H ₂ O
176s		Lattice modes		1974w	?
234m				2036w	
308s		v Zn–Cl		2176w	
402w	403m	ho CCN		2228w	
500m	502m	$ ho$ COO $^-$		2280w	
	555m	v Zn–O		2432w	
596w	603m	ω COO $^-$		2520m	
710w	708s	δ COO ⁻ , γ N–H(X)		2553m	
	904s	vs CCN		2645m	
911s	917m	$\rho \text{ CH}_2$		2737m	
1041s	1044m	v _{as} CCN		2826m	
1120m	1124m	$\rho \text{ NH}_3^+$		2909s	
1144m	1140m		2958 s	2958s	vs CH ₂
1313m	1310m	ω CH ₂		3000sb	v N–H(…O)
1339s	1343s	τCH_2	3017 m	3016s	v _{as} CH ₂
1405sh	1397s	v _s COO ⁻		3045sb	v N–H(…O)
	1411s		3070w		
1430m		δCH_2		3140sh	
1442s	1444s		3197w	3197s	
	1481m	$\delta_{s} \text{NH}_{3}^{+}$		3370s	
1519m	1519s		3340w		v N-H(X), v O-H(O)
1582m		$\delta_{as} \operatorname{NH_3}^+$	3435w		v O–H(…O)
	1603s			3449s	
1611m	1615sh				

219 and 215 °C, respectively. The glycine decomposition and oxidation of air atmosphere is inhomogeneous process and takes place in several steps – for 2Gly·ZnCl₂·2H₂O the maximums are at 260 and 294 °C (induced by ZnCl₂ melting); the most significant steps for Gly·ZnCl₂ are at 290 °C (induced by ZnCl₂ melting) and 317 °C; and for 3Gly·ZnCl₂ they are at 244 and 291 °C (induced by ZnCl₂ melting), respectively. The end of the process decomposition and oxidation depends on the glycine content in the three compounds. The highest temperature (582 °C) was registered for 3Gly·ZnCl₂ and the lowest, (462 °C), for Gly·ZnCl₂.

The process of ZnCl₂ melting is practically similar, with small temperature differences for the three compounds. For

the compound Gly-ZnCl₂ it is observable decomposition and oxidation of the rests of organics with maximum around 511 °C and simultaneous ZnCl₂ evaporation with maximums around 562, 594 and 634 °C and end at 690 °C (near ZnCl₂ boiling point). For the compound 3Gly-ZnCl₂ decomposition and burning of organic parts is finished around the temperature 582 °C. With rising of temperature the ZnCl₂ evaporates, and all effects are over at 720 °C. For 2Gly-ZnCl₂.2H₂O is observable ZnCl₂ evaporation with maximums around 541 °C, 567 °C and end at 705 °C.

In a conclusion, the lower thermal stability possesses 2Gly-ZnCl₂·2H₂O (up to 78 °C) in comparison with the anhydrous

Table 6	
FTIR and FT Raman spectra of	3Gly∙ZnCl ₂

FT Raman (cm ⁻¹)	$FTIR (cm^{-1})$	Assignment	FT Raman (cm ⁻¹)	$FTIR (cm^{-1})$	Assignment
155s		ρ CCN	1334m	1335sh	τ CH ₂
202m		lattice modes	1409s	1412s	v _s COO ⁻
261m			1417sh	1419s	
279s		v Zn–Cl		1426sh	
307m			1440m		δCH_2
362w		ρ CCN	1446sh	1447s	
490w	490w	ρ COO-	1486w		$\delta_{s} \text{ NH}_{3}^{+}$
514w	514m		1495w	1499s	
562w	561m	v Zn–O	1561w	1562s	$\delta_{as} \text{ NH}_3^+$
590m	595m	ω COO $^-$	1583m		
674w	674w	$\delta \text{ COO}^-$		1602s	
688w	688w		1615w		$v_{as} COO^-$
887m	887m	v_s CCN, γ N–H(X)	1631w		
901s	896m		1646w	1643s	
912s	919s	$\rho \text{ CH}_2, \gamma \text{ N-H}(\cdots \text{X})$		1944wb	?
930w	929m			2435m	
	934m			2531m	
1031m	1031m	v _{as} CCN	2620w	2615s	
	1035m			2694s	
1099w	1099m	$\rho \text{ NH}_3^+$		2810s	v N-H(O)
1113m	1112m		2880w	2877s	
1126m	1127m		2950sh		$v_{\rm s}$ CH ₂
1135m	1136m		2960s	2960s	
1301m	1300s	$\omega \operatorname{CH}_2$	2975sh		
1316s	1318s		3009s	3009s	v_{as} CH ₂
1321s	1325s	$\tau \ CH_2$	3175w	3180sb	v N-H(X)

Table 7

TG-DTA data interpretation of Gly-ZnCl_2, 3Gly-ZnCl_2, and 2Gly-ZnCl_2·2H_2O in (°C)

Compound	Phase transition/effect description	Data from DTA and TG				
		$T_{\rm max}$ (°C)	ΔT	Δ <i>m</i> , %		
				Calc.	Exp.	
Gly∙ZnCl₂	$Gly \cdot ZnCl_2 \rightarrow Gly \uparrow + ZnCl_2$					
	Glycine – melting	229				
	Glycine – decomposition	290, 317	229-462	-35.5	-32.1	
	$ZnCl_2$ – melting	290				
	ZnCl₂↑	511, 562, 594, 634	462-690	-64.5	-61.7	
3Gly ZnCl ₂	$3Gly \cdot ZnCl_2 \rightarrow 3Gly \uparrow + ZnCl_2$					
	Glycine – melting	219				
	Glycine – decomposition	244, 291	219-582	-62.3	-63.2	
	$ZnCl_2$ – melting	291				
	ZnCl₂↑	630	582-720	-37.7	-33.1	
2Gly·ZnCl ₂ ·2H ₂ O	2 Gly·ZnCl ₂ ·2H ₂ O \rightarrow 2Gly·ZnCl ₂ + H ₂ O \uparrow					
	Step I $\rightarrow -1.5H_2O$	104	78-120	-8.4	-8.7	
	Step II $\rightarrow -0.5H_2O$	138	120-194	-2.8	-2.5	
	$2 \text{ Gly} \cdot 2 \text{ nCl}_2 \rightarrow 2 \text{ Gly}^{\dagger} + 2 \text{ nCl}_2$					
	Glycine – melting	215				
	Glycine – decomposition	260, 294	217-501	-46.5	-47.1	
	$ZnCl_2$ – melting	294				
	ZnCl₂↑	541, 567	501-705	-42.3	-40.0	

compounds Gly-ZnCl_2 which is stable up to 229 °C and 3Gly-ZnCl_2 – up to 219 °C.

4. Conclusion

The coordination behaviour of Zn^{2+} ions in aqueous chlorideglycine solutions and the formation of mixed zinc complexes are responsible for the salt crystallization. The mixed complexes $[Zn(Gly)_2Cl_2]$ have been predicted to be predominating in these solutions and to be characteristic of the crystal structures of the crystallizing compounds. The crystal structures of the obtained compounds Gly·ZnCl_2, 2Gly·ZnCl_2·2H_2O and 3Gly·ZnCl_2 have been solved. The discrete tetrahedra $[Zn(Gly)_2Cl_2]$ are the main building units for 2Gly·ZnCl_2·2H_2O (monoclinic crystal system, space group C2/c) and for 3Gly·ZnCl_2 (orthorhombic crystal system, space group $Pna2_1$). Infinite chains of $[Zn(Gly)_{2/2}Cl_2]$ tetrahedra form $Gly \cdot ZnCl_2$ (monoclinic crystal system, space group $P2_1$).

Vibrational spectra of all three compounds were recorded, analyzed and assigned. The overall character of the spectra is in accord with refined crystal structures.

The close thermal behaviour found for the three compounds is also in accordance with their structural similarity.

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