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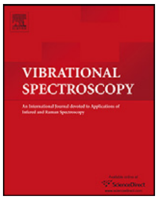

Raman spectroscopic and DSC studies of diglycine-perchlorate (DGPCl)

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ABSTRACT

Single crystals of diglycine perchlorate (DGPCl) and deuterated diglycine perchlorate (DDGPCl) are synthesized and studied using differential scanning calorimetry (DSC) and Raman spectroscopy. DSC data indicated that both DGPCl and DDGPCl undergo a reversible first-order phase transition (solid-solid) at −11.5 °C and −9.3 °C, respectively. The Raman spectra of DGPCl and DDGPCl obtained at ambient temperature are analyzed to infer on the strength of hydrogen bonding in this compound relative to the parent compounds. The occurrence of NH stretching frequency at higher value in DGPCl in comparison with glycine suggests presence of a weak N–H···O hydrogen bond in DGPCl than in glycine. The lower isotropic melting temperature of DGPCl as compared to that of glycine is understood on the basis of the relative strength of hydrogen bonding in these compounds.

1. Introduction

Glycine in the presence of different inorganic acids (*i.e.*, H_2SO_4, H_2SeO_4, HNO_3, and H_3PO_4) forms compounds which exhibit various types of structural phase transitions [1–4]. Some of the glycine compounds, triglycine sulfate (TGS), triglycine selenate (TGSe), diglycine nitrate (DGN), glycinium phosphite (GPI) and triglycine sulfophosphate (TGSP) being ferroelectric. These glycine compounds are molecular type crystals with glycine and oxygen-anion complexes (NO_3^- in DGN, SO_4^{2-} in TGS, SeO_4^{2-} in TGSe and $H_2PO_3^-$ in GPI) and undergo phase transition of the order–disorder type [1]. The hydrogen bonds are known to play a very important role in the structural phase transition of these compounds. In glycine compounds, TGS, TGSe, DGN, TGSP strong hydrogen bond exist between the carboxyl groups, which participate in the complex mechanism of the phase transition between the paraelectric and ferroelectric phases [5].

In search for new ferroelectric substances, addition compound of α-glycine with perchloric acid is synthesized and studied. Good quality, optically transparent single crystals of diglycine-perchlorate (DGPCl) are obtained when glycine and perchloric acid are taken in 2:1 molar ratio. Structure of this new adduct has been recently reported based on single crystal X-ray diffraction measurements [6]. DGPCl is also a hydrogen bonded compound similar to other glycine compounds, having a strong O–H···O hydrogen bond between glycine ions and a relatively weak N–H···O hydrogen bond [1–3]. The asymmetric unit of DGPCl crystal consists of five glycinium–monoprotonated glycinium dimers and five perchlorate anions. The crystal structure of DGPCl is stabilized by a three dimensional network of hydrogen bonds between the glycine and perchlorate ions. Hydrogen bonding in this compound is similar to that in other glycine compounds such as TGS and DGN, having a strong O–H···O hydrogen bond between glycine ions and a relatively weak N–H···O hydrogen bond with the perchlorate ions. At ambient temperature (25 °C) in all dimers the O–H and H···O distances are approximately 1.332 Å and 1.146 Å, respectively, *i.e.*, the hydrogen atom is located closer to the monoprotonated glycinium ion. Similar glycinium–monoprotonated glycinium dimers are present in TGS and DGN crystals [1–3]; however, in the case of DGPCl, the orientation of the CH_2 and the NH_3^+ groups with respect to the C–N bond axis are staggered while in TGS and DGN, these are planar [1–3,6]. One of the important differences between TGS and the title compound is that out of the three glycine ions in TGS, two forms the glycinium–monoprotonated glycinium dimer with the third glycine forming week hydrogen bonding with sulfate ion whereas in DGPCl (DGN), there are only glycine dimers weakly bound to the perchlorate (nitrate) ion. In order to understand the extent of various intermolecular interactions and their influence on the physical properties, Raman spectroscopic measurements and DSC studies were carried out on DGPCl. For an unambiguous identification of the vibrational bands associated with the amine group and the –COOH group, which play key role in the intermolecular hydrogen-bonding, partially deuterated compound, henceforth referred to as deuterated-DGPCl (DDGPCl) was also synthesized and investigated. In DDGPCl the hydrogen atoms in $-NH_3^+$ and –COOH groups are replaced by deuterium atoms to have $-ND_3^+$ and –COOD groups.

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2. Experimental

2.1. Crystal growth

Single crystals of diglycine perchlorate (DGPCl) were grown at 20 °C by the slow evaporation of the aqueous solution containing α-glycine and perchloric acid in 2:1 molar ratio. Good quality single crystals were obtained which were used to perform DSC and Raman experiments. Deuterated α-glycine (Dα-glycine) and DGPCl (DDGPCl) were obtained by re-crystallising α-glycine and DGPCl, respectively in D_2O repeatedly until complete deuteration of all the NH_3^+ and –COOH (to ND_3^+ and –COOD) groups, was confirmed using Raman spectroscopy. However, the Raman spectrum of deuterated glycine was found to resemble to that of Dγ-glycine.

2.2. Differential scanning calorimetry (DSC)

Mettler Toledo DSC 822 was used for thermal measurements of the samples, with an empty aluminum pan as a reference. Temperature and enthalpy calibration of the instrument were done, using cyclohexane and indium. The transition temperature, T_c, reported is the peak temperature. The transition enthalpy of the endothermic curve is calculated by using the software supplied by Mettler Toledo. The expected experimental errors in temperature and enthalpy values were ±0.1 °C and ±5%, respectively. For measuring (i) low temperature transition 25–30 mg crystal and (ii) crystal to isotropic melting 3–4 mg crystal was used. The DSC experiments were repeated many times with the (a) same sample to check the reversibility of the transitions and (b) fresh samples from different synthesis to check the reproducibility of the DSC data.

2.3. Raman spectroscopy

The Raman spectra were recorded using 532 nm laser line. Power on the sample was kept below 10 mW to reduce the radiation damage. Scattered light was detected using a CCD-based (Andor Technology) spectrograph consisting of a home-built 0.9 m monochromator together with a super notch filter. Entrance slit was kept at 50 μm which gives a spectral band pass of 3 cm^{-1}.

3. Results and discussions

3.1. Differential scanning calorimetry

DSC experiments of DGPCl were carried out to check the existence of any polymorphic transition besides the melting transition. The DSC heating thermograms in the temperature range −120 to 300 °C obtained with α-glycine, Dγ-glycine, DGPCl and DDGPCl are shown in Fig. 1a and b. On heating the samples in −120 to 30 °C temperature range, the DGPCl crystal shows an endothermic transition at temperature, T_c, −11.5 °C and the enthalpy, ΔH associated with this transition is 1.9 J g^{-1}. This transition is obtained in repeated cooling and heating cycle indicative of a reversible transition. The change in entropy $\Delta S = \Delta H(M/T)$ (where T is the transition temperature and M is the molecular weight) can be calculated using the value of enthalpy, ΔH obtained by integration of the anomalies in specific heat. The ΔS for the solid–solid phase transition is 9.20 J mol^{-1} K^{-1}. The transition entropy can be interpreted in terms of Boltzmann's equation $\Delta S = R\ln(N_1/N_2)$, where N_1 and N_2 are the numbers of respective orientations and R the gas constant. The calculated entropy, ΔS value is close to $R\ln 3$ pointing to order–disorder mechanism of the transition [7]. The DSC heating scan of partially deuterated diglycine perchlorate (DDGPCl) crystals also shows presence of solid–solid phase transition at temperature T_c, −9.3 °C and the enthalpy, ΔH associated with this transition is 1.8 J g^{-1}.

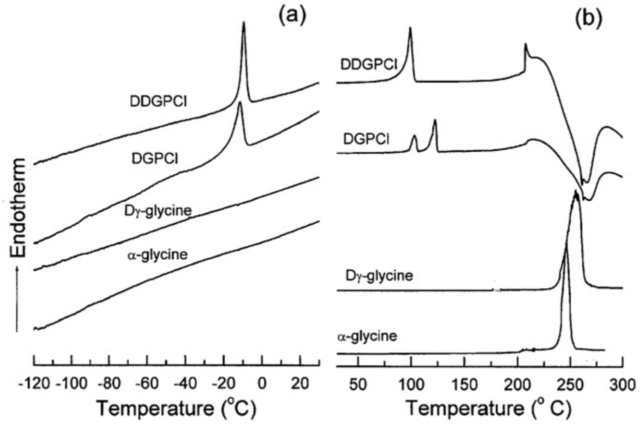

Fig. 1. DSC heating thermograms at 5 °C/min of α-glycine, Dγ-glycine, DGPCl and DDGPCl in (a) −120 to 30 °C and (b) 30–300 °C temperature range.

The DSC heating thermogram of the crystal to isotropic melting transition obtained with DGPCl is different from that of pure α-glycine, indicating formation of new compound (Fig. 1b). In pure α-glycine, the melting transition is seen at 246.5 °C and the enthalpy associated with this transition is 1026 J g^{-1}. However, the melting transition of DGPCl was complex consisting of multiple transitions at 103.5 °C, 123 °C and 216 °C. The enthalpy associated with these transitions is 285 J g^{-1} (total enthalpy). The compound on further heating decomposes as indicated by exothermic transition at 262.6 °C. Similar behaviour is observed with melting transitions of DDGPCl (Fig. 1b).

3.2. Raman spectroscopy

In a molecular crystal, the intramolecular potentials are generally weakly perturbed by the intermolecular interactions hence the internal vibrations of a molecule exhibit rather small variation in different crystalline environments. The mode assignment of DGPCl and DDGPCl compounds were carried out by comparing the Raman frequencies of their internal mode region to those observed in the parent compounds $HClO_4$, α-glycine and Dγ-glycine [8,9]. In some regions where there is overlap of Raman bands of different molecular units, assignments are made based on comparison with those reported for DGN or TGS [10–12]. The Raman spectra of perchloric acid, α-glycine, Dγ-glycine, DGPCl and DDGPCl at ambient temperature (25 °C) in 50–750 cm^{-1}, 750–1750 cm^{-1} and 1750–3800 cm^{-1} regions are shown in Figs. 2–4, respectively. The assignment for the different modes observed in these compounds is given in Table 1. The Raman shifts and assignments of most of the modes of α-glycine, Dγ-glycine, perchloric acid obtained in the present studies are consistent with those reported earlier (Table 1) [8,9,13,14]. On comparing the Raman spectrum of DGPCl with that of parent compounds (α-glycine, and perchloric acid) it is clearly seen that the various glycine bands are affected by complexation (Figs. 2–4).

3.2.1. The vibrations of ClO_4^- anion

According to Siebert [15] a free ClO_4^- anion with T_d symmetry has four fundamental vibrations, a non-degenerate symmetric stretching mode ν_1, a doubly degenerated bending mode ν_2 and the triply degenerate stretching (ν_3) and bending (ν_4) vibrations. In the present studies, the mode frequencies of ν_1, ν_2, ν_3, and ν_4 were obtained from the Raman spectrum of perchloric acid to be 933, 464, 1084 cm^{-1} and 630 cm^{-1}, respectively (Table 1). As the degeneracy is completely lifted in the triclinic crystalline environment, splitting of the degenerate internal modes of the ClO_4^- may be expected in DGPCl. Raman bands of ClO_4^- anion become narrow in DGPCl due to the reduced mobility of the ClO_4^- anion

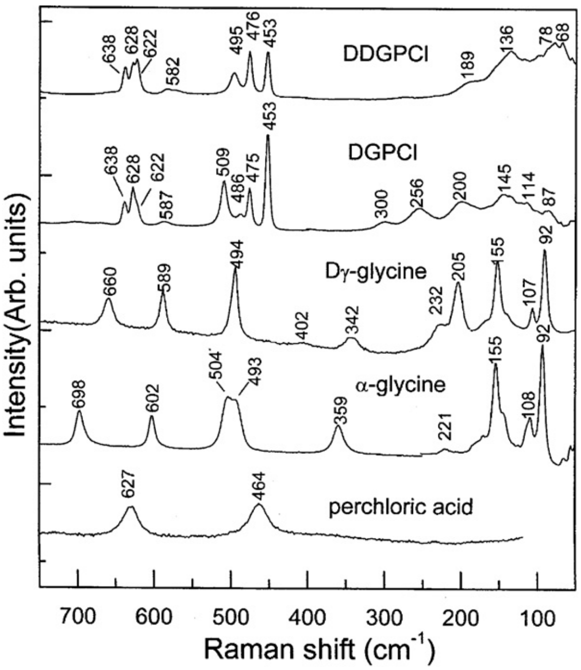

Fig. 2. Raman spectra of perchloric acid, α-glycine and Dγ-glycine, DGPCl and DDGPCl in 750–50 cm^{-1} region at 25 °C. In figure some bands are marked, while all bands are listed in Table 1.

ion in the perchlorate complex [16]. In the complex, the strongest mode at 933 cm^{-1}could be unambiguously identified to be due to ν_1 stretching vibration of the perchlorate ion. In the other regions, identification of the Raman modes is made by comparing the spectrum with those of DGN and TGS.

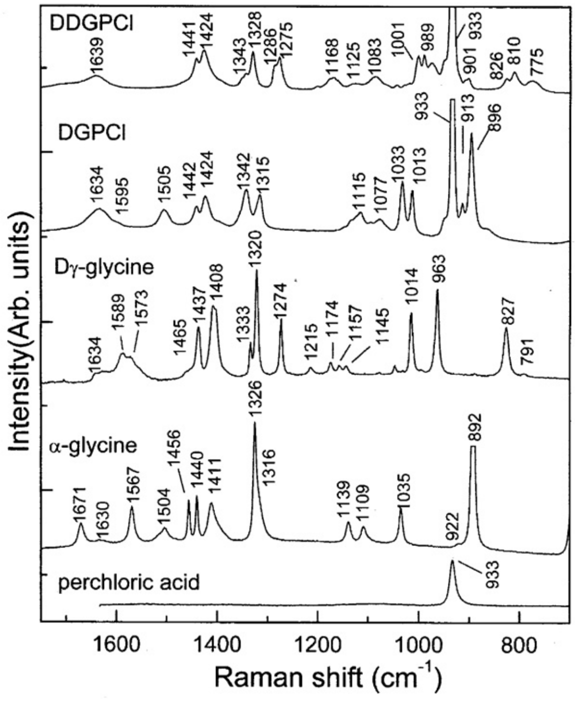

Fig. 3. Raman spectra of perchloric acid, α-glycine, Dγ-glycine, DGPCl and DDGPCl in the 1750–750 cm^{-1} region at 25 °C. In figure some bands are marked, while all bands are listed in Table 1.

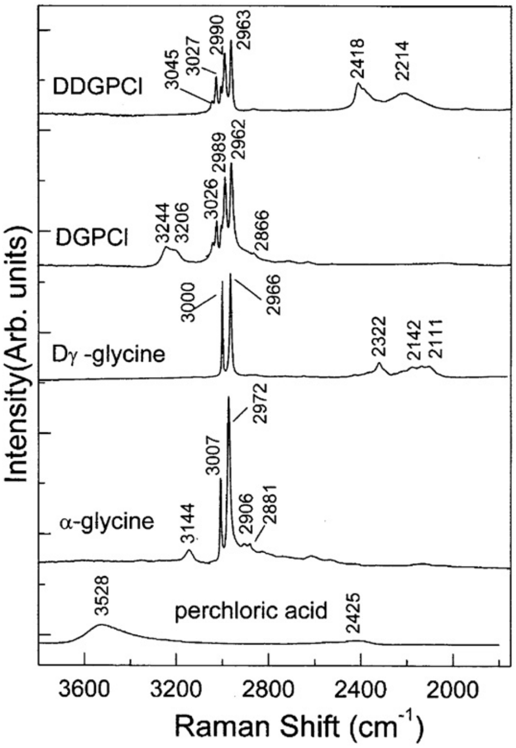

Fig. 4. Raman spectra of perchloric acid, α-glycine and Dγ-glycine, DGPCl and DDGPCl in the 3800–1750 cm^{-1} region at 25 °C. In figure some bands are marked, while all bands are listed in Table 1.

3.2.2. *The vibrations of glycine ions*

The relatively sharp and intense vibrational bands observed in 3050 cm^{-1} to 2800 cm^{-1} region of α-glycine spectrum are due to the C–H bonds of the CH_2 groups. In DGPCl, three doublets of ν_sCH_2 and $\nu_{as}CH_2$ are observed as compared to one doublet of ν_sCH_2 and $\nu_{as}CH_2$ in α-glycine [17]. This behaviour in DGPCl is similar to that reported in TGS compound [17], wherein the intensity ratio of the ν_sCH_2 and $\nu_{as}CH_2$ doublets are correlated with the presence of two different conformers of the glycine molecules [17]. Thus presence of three doublets of ν_sCH_2 and $\nu_{as}CH_2$ in DGPCl may be interpreted as due to the presence of three different conformers of glycine molecule. This can be understood from the structural date of DGPCl [6]. The crystal structure of DGPCl has been determined to be triclinic (space group P-1) with ten glycine moieties and five perchlorate ions (ClO_4^-) in an asymmetric unit. The diffraction data showed that these glycine moieties exist as dimers ($^+NH_3CH_2COOH\cdots{}^-OOCCH_2NH_3^+$) due to strong hydrogen bonding interaction between the zwitterionic ((G_{zw}) ($NH_3^+CH_2COO^-$)) and monoprotonated ((G_{mP}) ($NH_3^+CH_2COOH$)) glycine moieties (as shown in Fig. 5). There are five crystallographically non-equivalent glycine ($G_{zw} - G_{mP}$) dimers in an asymmetric unit of DGPCl crystal. The glycine dimers in DGPCl are similar to the one existing in TGS (GII–GIII) and DGN (G_A–G_B) crystals [1–3,12]. Presence of three sets of doublets in this spectral region of DGPCl may be interpreted as due to existence of three set of glycine molecules with different dihedral angle. This is supported by the crystallography data of DPGCl showing presence of four glycine molecules with average dihedral angle 19.62°, four glycine molecules with average dihedral angle 16.97° and two glycine molecules with average dihedral angle 15.97° [6]. The C–H stretching vibrations of DDGPCl occur at similar wave number and were not affected by deuteration as expected (Table 1). Raman bands due to O–H stretching vibration could not be distinctly observed in the present studies probably due to poor intensity of the band.

Table 1
Raman frequencies (cm^{-1}) and relative intensity (I_R)[a] of the bands observed in $HClO_4$, α-glycine, Dγ-glycine, DGPCl and DDGPCl and their assignments.

Assignments	$HClO_4$ (I_R)[a]	α-Glycine (I_R)[a]	Dγ-Glycine (I_R)[a]	DGPCl (I_R)[a]	DDGPCl (I_R)[a]
Lattice modes		55		56 (0.3)	56
		65		69 (0.1)	68 (0.5)
		92 (46)	92 (69)	87 (0.9)	78 (1)
		108 (12)	107 (19)	114 (2)	100
		142	139		118
		155	155 (56)	135 (3)	136 (6)
		171	170	145 (4)	
		186 (34)	205 (18)	200 (0.7)	189 (0.5)
		221 (2)	232	256 (0.2)	
C–CN bend		359 (11)	342 (3)	300 (0.1)	276
γ_{ClO_4} (ν_2)	464 (13)	–	–	453 (22)	453 (10)
ND_3 tor			402 (1)		
NH_3 tor		493 (20)	–	509 (11)	–
CO_2 rock		504 (20)	494 (16)	475 (10)	476 (11)
γ_{ClO_4}				486 (4)	495 (5)
CO_2 wag		602 (12)	589 (11)	587 (2)	582 (1)
$\delta_{s(ClO_4)}$	627 (12)			622 (5)	622 (8)
$\delta_{s(ClO_4)}$ (ν_4)	630 (11)			628 (10)	628 (8)
CO_2 bend		698 (14)	660 (7)	638 (6)	638 (6)
ND_3 rock			791/827 (2/28)		775/810/826 (2/3/2)
C–C s str		892 (100)	963 (51)	896/913 (21/8)	901/974 (2/1)
CH_2 rock		922			
$\nu_{s(ClO_4)}$ (ν_1)	933 (100)			933 (100)	933 (100)
C–N str		1035 (9)	1014 (37)	1013 (10)	9895 (5)
C–N str				1033 (13)	1001 (5)
$\nu_{as(ClO_4)}$ (ν_3)	1084 (5)			1080 (5)	1083 (2)
NH_3 rock		1109/1139 (4/6)		1077/1095 (5/4)	
NH_3 rock				1115/1135 (6/5)	
ND_3 s def			1145/1157 (4/5)		1085/1125 (2/1)
ND_3 s def			1174 (7)		1168 (2)
ND_3 as def			1215/1274 (4/33)		1275/1286 (5/4)
CH_2 twist		1316	1320 (62)	1315 (9)	1328 (6)
CH_2 wag		1326 (33)	1333 (20)	1342 (10)	1343 (2)
CO_2 s str		1411 (11)	1408 (44)	1424 (9)	1424 (6)
CH_2 bend		1440 (12)	1437 (32)	1442 (7)	1441 (5)
CH_2 sciss		1456 (11)	1465		
NH_3 s def		1504 (4)		1505 (7)	
CO_2 as str		1567 (10)	1573/1589 (17/14	1595 (4)	
C=O str and CH_2 wag		1630 (2)	1630 (7)	1634 (7)	1639 (2)
NH_3 as def		1671 (7)		1634 (7)	
ND_3 as str			2111/2142 (10/11		2214 (1)
ND_3 as str			2184/2322 (9/14)		2418 (8)
ClO_4	2425 (2)				
2x1440		2881 (6)	2860 (2)		
2x1456		2906 (6)	2880 (2)	2866 (2)	2869 (0.5)
CH_2 s str		2972 (77)	2966 (100)	2962 (11)	2963 (20)
CH_2 as str		3007 (38)	3000 (93)	2989/3006 (10/5)	2990/3007 (6/7)
CH_2 as str				3026/3043 (6/2)	3027/3045 (10/3)
NH_3 as str		3144 (5)		3206/3244 (2/3)	
OH str (ClO_4)	3528 (9)				

ν = str = stretching, bend = bending, tor = torsion, γ = rock = rocking, twist = twisting, ω = wag = wagging, δ = def = deformation, s = symmetric, as = asymmetric.

[a] Relative intensity of the band is given in 100 points scale (I_R = 100 corresponds to the strongest band).

Modes associated with the NH_3^+ show up distinctly in deuterated compounds while those that participate in the hydrogen bonding show shift in position correlating with the strength of hydrogen bonding. The broad stretching vibration of N–H bonds in α-glycine at 3144 cm^{-1} shift to 3244 cm^{-1} in DGPCl. The increase in the NH stretch frequency suggests weaker strength of N–H···O hydrogen bond in DGPCl as compared to that in glycine. This is because of different structures of the glycine ions in α-glycine and DGPCl. In DGPCl crystal two glycine ions G_{zw} and G_{mP} are present as dimer and the N–H···O hydrogen bonding interactions are with ClO_4^- anion. While in α-glycine the N–H···O hydrogen bonding interactions is with $-NH_3^+$ and $-COO^-$ group of adjacent glycine molecules. On deuteration, NH-stretch bands shift to lower frequencies and are observed at 2214, 2390 and 2416 cm^{-1}. The shapes of these bands are similar to those observed in the spectrum of the non-deuterated DGPCl. In DGPCl only one NH stretch band is distinctly observed as the weak lower frequency NH stretch band probably overlap with the intense C–H stretching bands.

On comparing the DGPCl bands in 1800–200 cm^{-1} region with the corresponding bands in α-glycine, Dγ-glycine and DDGPCl it is inferred that the broad band at 1634 cm^{-1} may be assigned to (ν(C=O), wag (CH_2) and NH_3^+ def$_{as}$) in DGPCl. The 1505 cm^{-1} band may be assigned to NH_3^+ def$_s$ which is not seen in DDGPCl. The CO_2 stretching at 1411 cm^{-1} seen in α-glycine is shifted to 1424 cm^{-1} in both DGPCl and DDGPCl. The bands at 1342 cm^{-1} (1343 cm^{-1}) and 1315 cm^{-1} (1328 cm^{-1}) can be assigned to CH_2 wagging and CH_2 twisting in DGPCl (DDGPCl), respectively. The CH_2 wagging band shows an increase in frequency when compared to corresponding glycine band. In DDGPCl new bands are seen at 1286 cm^{-1} (with shoulder at 1275 cm^{-1}) and at 1085, 1125, and 1168 cm^{-1} probably corresponding to ND_3 def$_{as}$ and ND_3 def$_s$, respectively. Similar shift in ND_3 def$_{as}$ and ND_3 def$_s$ bands was reported in Dα-glycine [13]. The bands at 1077 cm^{-1}, 1095 cm^{-1}, 1115 cm^{-1} and 1083 cm^{-1} can be assigned to NH_3 rocking, overlapping with the ClO_4^- asymmetric stretching bands. These ND_3 rocking bands appear at 775 cm^{-1}, 810 cm^{-1}, 826 cm^{-1} in DDGPCl spectrum. The NH_3 rocking bands

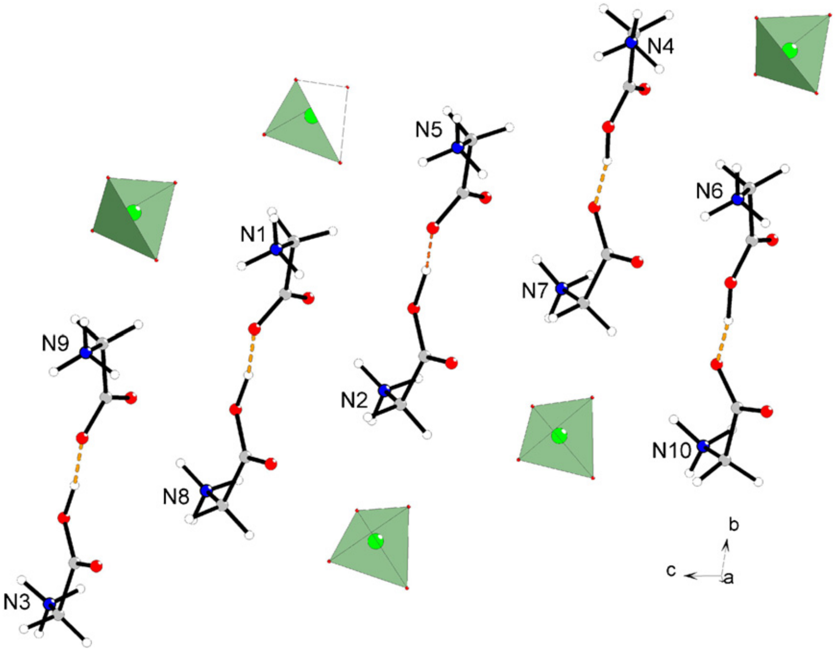

Fig. 5. Asymmetric unit of DGPCl crystal showing glycine dimers and perchlorate ions [6].

show decrease in the frequency when compared to corresponding glycine band. The 1033 cm^{-1} and 1013 cm^{-1} band are assigned to C–N stretching, corresponding to two types of glycine molecules. Similar behaviour is also seen in TGS [18]. However in DGPCl these bands are well resolved as compared to TGS. The broadened CO_2 bending and wag bands are seen at 638 cm^{-1} and 587 cm^{-1} with reduced intensity and frequency. These bands are not perturbed by deuteration. The CO_2 rocking at 475 cm^{-1} shows a decrease in frequency and NH_3 torsion at 509 cm^{-1} shows an increase in frequency in DGPCl when compared to glycine. In DDGPCl, the CO_2 rocking band occurs at same frequency as in DGPCl. However, the ND_3 torsion band shifts to a lower frequency. The C–C–N bending band in DGPCl (DDGPCl) is broadened and shifted to 300 cm^{-1}. The region below 250 cm^{-1} gives typical bands pertaining to the lattice modes (translational). Additional bands due to deformation modes of the glycinium skeleton, hindered rotation of the $NH_3(ND_3)$ groups and low frequency vibrations of the hydrogen bonds are also seen. However, the assignment is difficult in this region with the existing data.

In summary, the vibrational spectrum of DGPCl, which directly reflect the intra- and inter-molecular interactions correlate well with the structural data. Further, the relative strength of hydrogen bonding as compared to that in glycine, inferred from the spectroscopic studies, are in agreement with the high transition temperature and the enthalpy values of the isotropic melting of α-glycine than DGPCl. Further, in DGPCl, the three dimensional crystal structures is formed by hydrogen bond interaction between NH_3^+ group of glycine ions and Cl–O group of perchlorate anions. These hydrogen bond interactions are relatively weak probably leading to a dynamically disordered perchlorate anion at ambient temperature. The transition seen in DSC at low temperature can be possibly due to ordering of the perchlorate anions and glycine dimers.

4. Conclusions

Diglycine perchlorate (DGPCl), an organic–inorganic adduct, has been obtained using 2:1 molar ratio of α-glycine and perchloric acid and studied using differential scanning calorimetry (DSC) and Raman spectroscopy. DGPCl undergoes a reversible first-order phase transition at −11.5 °C. The entropy value obtained suggests an order-disorder type of transition. The Raman spectra of DGPCl and its deuterated analogue, DDGPCl were obtained at ambient temperature. Most of the vibrational bands of DGPCl could be assigned by making use of the known Raman assignments of the parent compounds, TGS and the Raman spectrum of deuterated DGPCl. The increase in the NH stretch frequency in Raman spectra of DGPCl suggests presence of a weak N–H···O hydrogen bond in DGPCl than in glycine. This week hydrogen bonds of N–H···O type with NH_3^+ cations and ClO_4^- anions could be resulting in disordered perchlorate anion. The anomaly in the heat flow at −11.5 °C observed in DSC scan can be associated with the ordering–disordering of the perchlorate anions.

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