STUDIES OF THE INFRARED SPECTRA OF DIGLYCINE BARIUM CHLORIDE MONOHYDRATE

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ABSTRACT

The studies of the infrared spectra of the equilibrium mixtures of diglycine barium chloride monohydrate, $(NH_3^+ CH_2COO^-)_2\ BaCl_2H_2O$ *containing the species*

(i) $(NH_3^+CH_2COO^-)_2.BaCl_2\ H_2O$
(ii) $(NH_2D^+CH_2COO^-)_2.BaCl_2.HDO$
(iii) $(NHD_2^+CH_2COO^-)_2\ BaCl_2\ HDO$
(iv) $(ND_3^+CH_2COO^-)_2\ BaCl_2\ D_2O$

have shown a strong coupling among different vibrations. The progressive changes in the intensities of the infrared absorption bands due to different equilibrium species are observed. These studies have also shown that some of the assignments of Laulicht et al. *are not in accordance with the observed results.*

1. INTRODUCTION

Glycine exists in the form of zwitter ion in the crystalline state as well as in the addition compounds with inorganic salts. Numerous investigations on the Raman and infrared spectra of α-glycine have been carried out[1-4]. Suzuki *et al.*[2] have made a normal coordinate analysis, considering the NH_3^+/ND_3^+ group as a mass point. Though there is general agreement between the calculated and observed frequencies, discrepancies found in the case of certain vibrations could be traced to the coupling of these modes with some of the vibrational modes of NH_3^+/ND_3^+ groups. This has been confirmed by the studies of the infrared spectra of the equilibrium mixtures of α-glycine[3]. Recently, Laulicht *et al.*[4] have reassigned some of the vibrations on the basis of their shifts in the infrared spectra of 180 labelled glycine. Many of these reassignments do not seem to be compatible with the data available. Hence an infrared study on the equilibrium mixtures of diglycine barium chloride monohydrate was undertaken to examine the correctness of the reassignments and also to find out the nature of coupling of vibrations in the addition compounds.

2. EXPERIMENTAL DETAILS AND RESULTS

The equilibrium mixture of diglycine barium chloride monohydrate, $(NH_3^+CH_2COO^-)_2.BaCl_2.H_2O$ $[DGBaCl_2.H_2O]$ were obtained by dissolving $DGBaCl_2.H_2O$ inwater containing O, 33, 66 and 99 per cent D_2O. The solutions were stored in sealed tubes at 50°C for 3 days and then evaporated over P_2O_5 in a vacuum desiccator. The samples thus obtained contain the following species in various proportions.

(i) $(NH_3^+CH_2COO^-)_2\ BaCl_2\ H_2O$

(ii) $(NH_2D^+CH_2COO^-)_2.BaCl_2.HDO$

(iii) $(NHD_2^+CH_2COO^-)_2.BaCl_2\ HDO$ and

(iv) $(ND_3^+CH_2COO^-)_2.BaCl_2.D_2O$

The infrared spectra of the equilibrium mixtures were recorded with a double beam automatic infrared spectrometer, Carl-Zeiss UR-10 by KBr pellet technique. The absorption curves are reproduced in Figures 1 and 2 and the infrared frequencies for the four equilibrium mixtures are given in Table 1.

TABLE 1

Infrared Frequencies of the Equilibrium Mixtures of $DGBaCl_2.H_2O$ (Cm^{-1})

Sample 1	*Sample 2*	*Sample 3*	*Sample 4*	*Assignments*
NH_3/ND_3 group vibrations				
	1128 (s)	1128 (w)		Rocking
1126 (vs)	1100 (w)	1096 (w)	1096 (w)	
	818 (w)	818 (w)		
	848 (m)	848 (s)		
	770 (w)	767 (s)	844 (vs)	
	782 (w)		767 (vs)	
1480	1495 (s)	1495 (m)	1492 (w)	Bending
1500 (vs)				
1580				
1600 (vs)				
	1160 (m)	1160 (s)	1158 (vs)	
	1185 (m)	1178 (s)	1174 (vs)	
	1194 (vs)	1188 (m)	1186 (m)	
		1195 (w)	1194 (m)	
500				Torsion

TABLE 1—(*contd.*)

Sample 1	*Sample 2*	*Sample 3*	*Sample 4*	*Assignments*
CH_2 group vibrations				
905 (vs)	905 (s)	905 (m)	902 (w)	Rocking
	980 (w)	970 (w)	968 (m)	
	996 (vw)	996 (w)	993 (m)	
1306	1260 (w)	1260 (w)	1258 (m)	Twisting
	1278 (w)	1280 (w)	1273 (m)	
1340	1332 (s)	1332 (vs)	1330 (vs)	Wagging
	1346 (s)	1345 (sh)		
1448	1450 (vs)	1445 (vs)	1444 (vs)	Scissoring
		1465 (sh)	1460 (vs)	
COO^- group vibrations				
508 (vs)	503 (vs)	498 (vs)	493 (vs)	Rocking
583 (w)	583 (w)	583 (w)	580 (w)	Wagging
670 (vs)	644 (m)	642 (s)	638 (vs)	Bending
	656 (s)	656 (m)		
	670 (m)	670 (sh)		
1405	1390 (vs)	1388 (vs)	1388 (vs)	Sym. stretching
1425 (vs)	1425 (vs)	1420 (vs)	1420 (vs)	
1610 (vs)	1610 (vs)	1610 (vs)	1610 (vs)	Asym. stretching
H_2O group vibrations				
3455 (vs)	3455 (s)	3456 (sh)		Stretching
	3478 (s)	3476 (s)	3476 (s)	
3505 (vs)	3505 (s)	3500 (sh)		
	2525 (m)	2525 (s)	2526 (s)	
	2560 (vs)	2560 (vs)	2560 (s)	
	2602 (s)	2606 (s)	2610 (vs)	

3. DISCUSSION

Diglycine barium chloride monohydrate is orthorhombic space group V_h^{16}–Pnma[5]. The intra and intermolecular coupling in glycine addition compounds has been shown to be negligible[3]. The observed spectrum is therefore analysed in terms of the vibrations of glycine [CH_2 COO^-, NH_3^+/ND_3^+ and the skeletal (CCN^+) group vibrations all of which are Raman and infrared active] and those of water of crystallization, taking into account the possible coupling of vibrations. Many of the earlier assignments have been confirmed by the normal coordinate analysis[2] and are indicated in Table 1.

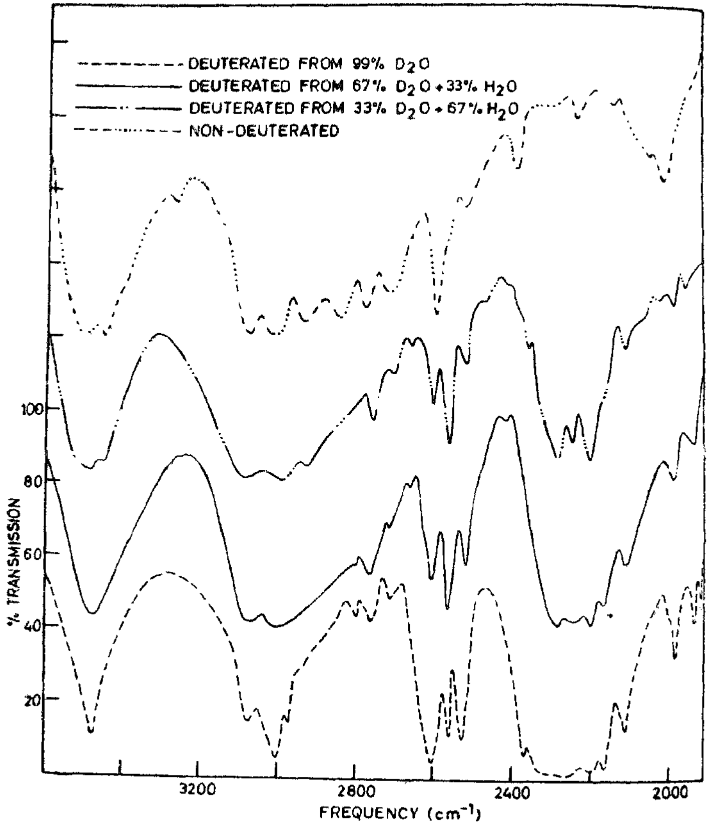

FIG. 1

IR Spectrum of DGFaCl_2-H_2O in K Br Pellet.

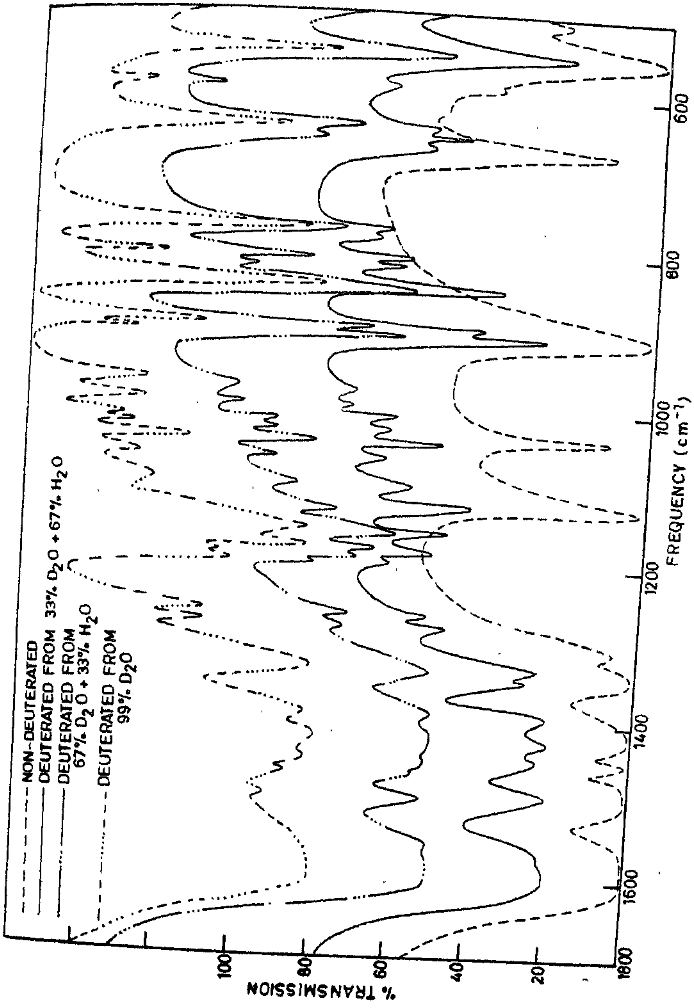

FIG. 2

IR Spectrum of DGBaCl$_2$·H$_2$O in KBr Pellet

Vibrations of CH_2 Group: In the Raman spectra of glycine and glycine addition compounds two or three sharp Raman lines have been observed in the region 2950 – 3050 cm^{-1} [1,6]. Two almost equally intense and sharp Raman lines have been observed at 2970 and 3000 cm^{-1} in the Raman spectra of $DGBaCl_2.H_2O$ and deuterated $DGBaCl_2$. On the other hand, in the infrared spectrum of $DGBaCl_2.H_2O$, the bands due to CH_2 stretching vibrations are hidden in the strong absorption bands due to H-bonded NH^+ stretching vibrations, as in the case of glycine[2,3]. Only in the case deuterated $DGBaCl_2$ two strong bands at 3000 and 3070 cm^{-1} with a shoulder at 2970 cm^{-1} could be seen (Fig. 1). On the other hand, Laulicht *et al*[4], from the infrared study of ^{18}O labelled glycine, have assigned the bands observed at 2830 and 2915 cm^{-1} to the stretching vibrations of the CH_2 group, while the calculated frequencies are 2960 and 3012 cm^{-1} [2]. The Raman lines observed in the region 2800 – 2950 cm^{-1} in the case of glycine and glycine addition compounds are diffused and weak and as such must be due to H-bonded NH^+ stretching vibrations.[1,6] Thus the present observation confirms the earlier assignments of Suzuki *et al.*

A strong band at 1448 cm^{-1} due to CH_2 scissoring shifts slowly to 1444 cm^{-1} on progressive deuteration and a new component appears at 1460 cm^{-1}. The CH_2 wagging mode at 1340 cm^{-1} shifts by 10 cm^{-1} on complete N-deuteration. The calculated frequencies of CH_2 twisting mode is 1270 cm^{-1}, while it has been observed at 1313 cm^{-1} in the case of α-glycine due to its coupling with the NH_3^+ rocking vibration[2]. In the absence of such a coupling *i.e.*, in the spectrum of N-deuterated glycine, it appears at 1270 cm^{-1}. In the present case, the spectrum of deuterated $DGBaCl_2$ shows two bands at 1258 and 1273 cm^{-1}.

The rocking mode at 910 cm^{-1} exhibits an unusual behaviour. This very intense band disappears on deuteration and two fairly intense bands are observed at 968 and 993 cm^{-1}. These bands have been assigned to CH_2 rocking modes in analogy with the assignment of the infrared band observed at 960 cm^{-1} in the spectrum of N-deuterated glycine[2].

COO^- Vibrations: In the infrared spectrum of $DGBaCl_2.H_2O$, the asymmetric and symmetric COO^- stretching vibrations are found to be doubled; though the two components due to COO^- asymmetric stretching are not resolved in the spectrum at room temperature. However, the existence of two components has been confirmed by the Raman effect studies and also in the infrared spectrum at 100°K.[7] On deuteration, the symmetric stretching vibrations are most affected, especially the one with the lower frequency, which shifts to lower frequencies by about 20 cm^{-1}.

The COO^- bending mode observed at 670 cm^{-1} for the normal salt is observed at 656, 644 and 638 cm^{-1} for the species (ii), (iii) and (iv) respectively. The progressive changes in the intensities of the bands at 670, 656, 644 and

638 cm^{-1} on successive deuteration can be seen from the curves in Fig. 2. The COO$^-$ wagging mode at 583 cm^{-1} is very little affected on N-deuteration. The band observed at 892 cm^{-1} in α-glycine, assigned to C-C stretching vibration by Suzuki *et al.*, has been reassigned to COO$^-$ bending on the basis of its shift on ^{18}O substitution[4]. However, on closer examination of the potential energy distribution table compiled by Suzuki *et al.*, one notices that the mode at 700 cm^{-1} assigned previously to COO$^-$ bending, contributes appreciably to the mode at 892 cm^{-1}. Thus the shift of about 20 cm^{-1} observed for the skeletal mode at 892 cm^{-1} on ^{18}O substitution appears to be justified. Secondly, Laulicht *et al.* have reassigned the band with a frequency of 502 cm^{-1} to NH_3^+ torsion. This is also not correct, though the absorption band due to the NH_3^+ torsion overlaps the band in question. This band in the case of $DGBaCl_2.H_2O$ shifts from 508 cm^{-1} to 493 cm^{-1} on complete N-deuteration, a shift of only 15 cm^{-1} as against a shift of about 100 cm^{-1} expected for NH_3^+ torsion. Thus the present study confirms the assignments of Suzuki *et al.* of the absorption bands at 892, 670 and 508 cm^{-1} to C-C stretching, COO$^-$ bending and COO$^-$rocking vibrations respectively.

NH_3^+/ND_3^+ vibrations: The NH_3^+ stretching region is very complex. In the pellet spectrum, a number of strong bands have been observed in the region 2600 – 3200 cm^{-1}, together with three sharp bands of medium intensity in the region 2200 – 2500 cm^{-1}. On partial deuteration, at first, three bands appear at 2210, 2250 and 2290 cm^{-1} and finally, a broad band in the 2150 – 2400 cm^{-1} results as can be seen from Fig. 1. These frequencies corresponding to these bands thus show a isotope shift by a factor of 1.3 due to mass effect. A few weak bands are still present in the region 2700 – 2900 cm^{-1} of the spectrum of deuterated $DGBaCl_2$ due to overtones and combinations of CH_2 deformation and COO$^-$stretching vibrations. These observations support the conclusion that for a better explanation of the observed features in the NH^+ stretching region, all the three mechanisms namely, the Stepanov's hypothesis, the combination hypothesis and the fundamental hypothesis must be considered simultaneously.[7]

The spectrum of $DGBaCl_2.H_2O$ exhibits two infrared bands, one sharp band at 1490 cm^{-1} and one broad band in the region 1550 – 1600 cm^{-1} due to NH_3^+ symmetric and degenerate bending vibrations respectively. On the other hand, the spectrum of deuterated $DGBaCl_2$ shows four bands due to ND_3^+ deformation vibration instead of 2 or 3 that one would normally expect. The NH_3^+ rocking vibration at 1126 cm^{-1} disappears on N-deuteration. Two intense bands observed at 844 and 767 cm^{-1} with an isotope shift ratio of 1.33 and 1.42 respectively, are assigned to ND_3 rocking vibrations. A similar observation has been made in the case of amino acids.[8]

Skeletal (CCN^+) vibrations: Instead of a single band at 1030 cm^{-1} in in the spectrum of the normal salt due to C – N stretching, a group of bands has been observed in the region 1000 – 1100 cm^{-1} on deuteration, a characteristic feature exhibited by other amino acids as well[8]. In the infrared spectrum of α-glycine a strong band due to C–C stretching at 892 cm^{-1} disappears completely on N-deuteration and a weak band observed at 1000 cm^{-1} has been assigned to this vibration by Suzuki *et al.* On the other band, in the case of $DGBaCl_2.H_2O$, the position and intensity of this band do not change on deuteration, indicating that in $DGBaCl_2.H_2O$ the C–N stretching vibration is not coupled to any other mode.

H_2O Vibrations: In the spectrum of $DGBaCl_2.H_2O$ two strong bands are observed at 3455 and 3505 cm^{-1} due to the stretching vibrations of the water molecule. On partial deuteration, three absorption peaks appear at 2525 (*m*), 2560 (*s*) and 2605 cm^{-1}. On further deuteration, the bands at 2525 and 2605 cm^{-1} gain in intensity and a single sharp absorption band is observed in the O–H stretching region. The bands observed at 2525 and 2605 cm^{-1} are due to D_2O stretching vibrations, while the bands observed at 2560 and 3476 cm^{-1} are due to the stretching vibrations of HDO group.

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