

Clathrate and Inclusion Compounds. Part 13 [1]. Vibrational and NMR Spectroscopic Studies of Carboxylic Acid Guests in Urea

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Abstract. Infrared, Raman and solid state ^{13}C NMR spectra have been recorded for a range of inclusion compounds of urea containing straight chain aliphatic carboxylic acids (butyric – decanoic) as guests. Inclusion compounds are not formed with formic, acetic and propionic acids. Thiourea does not form inclusion compounds with any of the C1 to C10 acids. The vibrational and NMR data support the conclusion that the acids are present as hydrogen bonded dimers in the channels of the host. The alkyl chain ^{13}C chemical shift values are very different from those of acid guests in the cavities formed in Dianin's compound. These suggest that the alkyl chains are present in the all-trans conformation, although weak bands observed in the spectrum of the decanoic acid inclusion compound lend some support to suggestions based on MM calculations that other conformations might be present.

Key words: IR spectroscopy, Raman spectroscopy, ^{13}C MAS NMR spectroscopy, clathrates, inclusion compounds, carboxylic acids, urea, thiourea.

1. Introduction

Inclusion compounds formed by urea and thiourea, first discovered in the 1940s, continue to attract much attention. Their characteristic structural feature is a long channel-like void in which guest molecules can be accommodated. As the channel diameter differs between urea and thiourea these two hosts have the ability to separate straight chain and branched chain alkanes. Thiourea also displays a remarkable selectivity for the axial rather than the equatorial conformer of monohalocycloalkanes. For both compounds their structures when acting as hosts differ from that of the polymorph stable in the absence of guest [2].

Most vibrational spectroscopic work on urea inclusion compounds containing carboxylic acids has concentrated on long chain fatty acids as guests [3], with a few reports on the study of short chain acid guests [4]. As carboxylic acids have been reported to form head-to-head dimers in the urea channels [5] their spectra can be compared with those of acid guests in hosts such as Dianin's compound [1] and deoxycholic acid [6]. Here we report on a study of the inclusion compounds formed between urea and thiourea with straight chain carboxylic acids using infrared (IR),

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Raman and solid state ^{13}C NMR spectroscopy. The data are compared with those from other systems containing carboxylic acids as guests.

2. Experimental

2.1. PREPARATIONS OF THE INCLUSION COMPOUNDS

The inclusion compounds were prepared by adding the acid to a saturated methanolic solution of the host. The solids were filtered, washed with ether and dried thoroughly in a desiccator before use.

2.2. CHARACTERIZATION TECHNIQUES

2.2.1. *Chemical Analysis*

The host : guest ratios of the samples were obtained using three methods:

Titrimetric analysis: about 0.5 g of the inclusion compound was dissolved in 50 mL ethanol and the liberated acid titrated with 0.02 M NaOH. Blank analysis was performed using 50 mL ethanol.

Thermal analysis: about 0.3 g of the inclusion compound was heated on an oil bath to 190°C and the weight loss determined. For the high boiling point acids the sample tube was evacuated. IR spectroscopy was used to check that all the guest had been liberated on heating. Blank analysis was performed using the host alone.

Elemental analysis was performed using a Carlo-Erba 1106 Analyser.

2.2.2. *IR and Raman Spectroscopy*

IR spectra of liquids and KBr discs ($4000\text{--}200\text{ cm}^{-1}$) were recorded on a Nicolet MX-10 FT spectrometer and transformed at 2 cm^{-1} resolution. Low temperature IR spectra of KBr discs were obtained using a Beckman VLT-2 variable temperature accessory. The Raman spectra were recorded using Ar^+ 514.5 nm excitation (Spectra Physics 164 laser) on a Cary 81 spectrometer modified as detailed elsewhere [7] using a slit width of 3 cm^{-1} .

2.2.3. *NMR Spectroscopy*

The CP ^{13}C solid state NMR spectra were recorded on a Varian VXR spectrometer operating at 75.43 MHz at the University of Durham. Depending on the sample the spinning rate was 3–4 kHz with 200 acquisitions. Liquid and solution phase spectra of the acids were recorded on a JEOL FX-100 FT NMR spectrometer operating at 25.05 MHz.

Table I. Host:guest ratios for the urea carboxylic acid inclusion compounds

Guest	Titrimetry	CHN analysis	Thermal analysis	Mean value
Formic acid	50.0	14.0	7.0	24
Acetic acid	40.0	100	22.0	54
<i>n</i> -Propionic acid	125	100	19.0	81
<i>n</i> -Butyric acid	18.0	13.7	9.0	13.6
<i>n</i> -Valeric acid	5.0 (5.4)*	4.7	4.7	4.8
<i>n</i> -Hexanoic acid	5.6 (6.0)	5.1	6.5	5.7
<i>n</i> -Heptanoic acid	6.3 (6.6)	5.8	6.6	6.2
<i>n</i> -Octanoic acid	6.3 (7.6)	5.9	7.9	6.7
<i>n</i> -Nonanoic acid	7.3 (8.2)	6.6	9.5	7.8
<i>n</i> -Decanoic acid	9.5 (8.9)	7.9	8.5	8.6

* Values reported by Schlenk [14].

3. Results and Discussion

3.1. HOST:GUEST RATIOS

Table I summarises the host:guest ratios obtained using the different analytical techniques. The data confirm previous studies that there is a lower limit on the alkyl chain length (3 carbon atoms) in order to stabilise the hexagonal polymorph of urea. No evidence was obtained for the formation of inclusion compounds between thiourea and the carboxylic acids.

3.2. INFRARED AND RAMAN SPECTRA

Although the different polymorphs of urea and thiourea give distinct vibrational spectra, Raman spectroscopy has been shown to be the better distinguishing technique due to the large difference between the $\nu(\text{C—N})$ band position of tetragonal (1014 cm^{-1}) and hexagonal (1028 cm^{-1}) urea [8]. The IR bands are broader as they are more affected by hydrogen bonding. The Raman data support the analytical results that inclusion compounds are not formed with formic, acetic and propionic acids. Furthermore the Raman spectra of the butyric acid preparations clearly show that mixtures of tetragonal urea and the inclusion compound have been formed. Comparison of the Raman spectrum of tetragonal urea with that of the octanoic acid inclusion compound (Figure 1) illustrates the differences between the spectra of the two polymorphs. The only guest molecule bands which can be observed are those arising from the $\nu(\text{CH})$ and $\delta(\text{CH}_2)$ modes. As reported for the Raman spectra of carboxylic acid guests in Dianin's compound [1] the carbonyl stretching band is very weak.

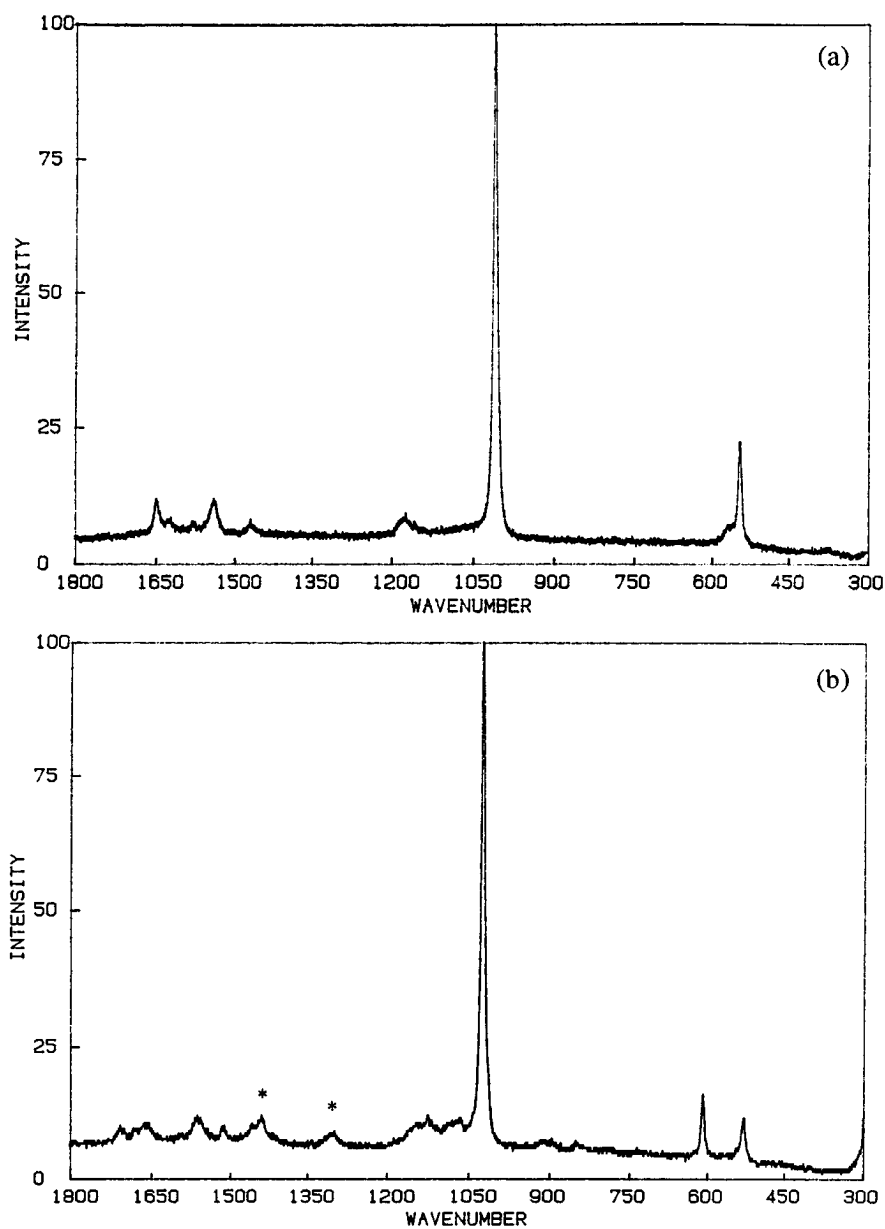


Figure 1. The Raman spectra (1800–300 cm^{-1}) of (a) tetragonal urea (b) the octanoic acid inclusion compound. Guest bands marked *.

Although the guest $\nu(\text{C}=\text{O})$ band overlaps with the host carbonyl band they can be distinguished in the IR spectrum (Figure 2). A single guest $\nu(\text{C}=\text{O})$ band is observed in all cases, in contrast to the spectra of the acids in Dianin's compound

Table II. IR carbonyl stretching values (cm^{-1}) for carboxylic acids.

Acid	Liquid phase	Guest RT	Guest 93 K
<i>n</i> -Valeric acid	1709	1716	1716
<i>n</i> -Hexanoic acid	1712	1716	1717
<i>n</i> -Heptanoic acid	1711	1716	1718
<i>n</i> -Octanoic acid	1712	1716	1717
<i>n</i> -Nonanoic acid	1711	1717	1718
<i>n</i> -Decanoic acid	1711	1717	1718

where multiple guest carbonyl bands were observed [1]. The values (Table II) are very close to the liquid phase values suggesting that short alkyl chain carboxylic acids, like the long chain acids [3], form head-to-head dimers in the channels. The low temperature IR spectra are much better resolved than the room temperature spectra (Figure 2c). Two effects must be considered in interpreting the low temperature spectra: those of temperature and the possibility of low temperature phase transitions. Such phase transitions have been reported for inclusion compounds containing other guest molecules where the low temperature phase of the urea host has an orthorhombic structure [2]. The guest carbonyl bands do not change significantly on decreasing the temperature suggesting no great change in the strength of the intermolecular hydrogen bond. The most significant difference is observed in the $1200\text{--}1350\text{ cm}^{-1}$ region where the CH_2 wagging band progression is clearly observable at 93 K. This progression is not observed in the liquid phase spectrum of the acid and arises from the ordered arrangement of the alkyl chain, with the host probably in the orthorhombic modification [3].

3.3. SOLID STATE ^{13}C NMR SPECTRA

Solid state NMR spectroscopy is a powerful analytical technique which, unlike X-ray crystallography, does not require single crystals. It has been applied to a wide range of host-guest systems [9]. As the hexagonal urea host displays just one band at ~ 164 ppm in the ^{13}C MASNMR spectrum the resonances due to the guest can be clearly observed (Figure 3). The chemical shift values of the guest resonances are given in Table III.

3.3.1. Guest Carbonyl Resonances

The ^{13}C chemical shift values of the guest carbonyl bands are very similar to those in the liquid phase, supporting the contention that the acids form head-to-head dimers in the channels. These values are similar to those of acid guests in the deoxycholic acid host [6] but very different from the chemical shift values of the carbonyl group of acid guests in Dianin's compound [1]. In the latter case the guest

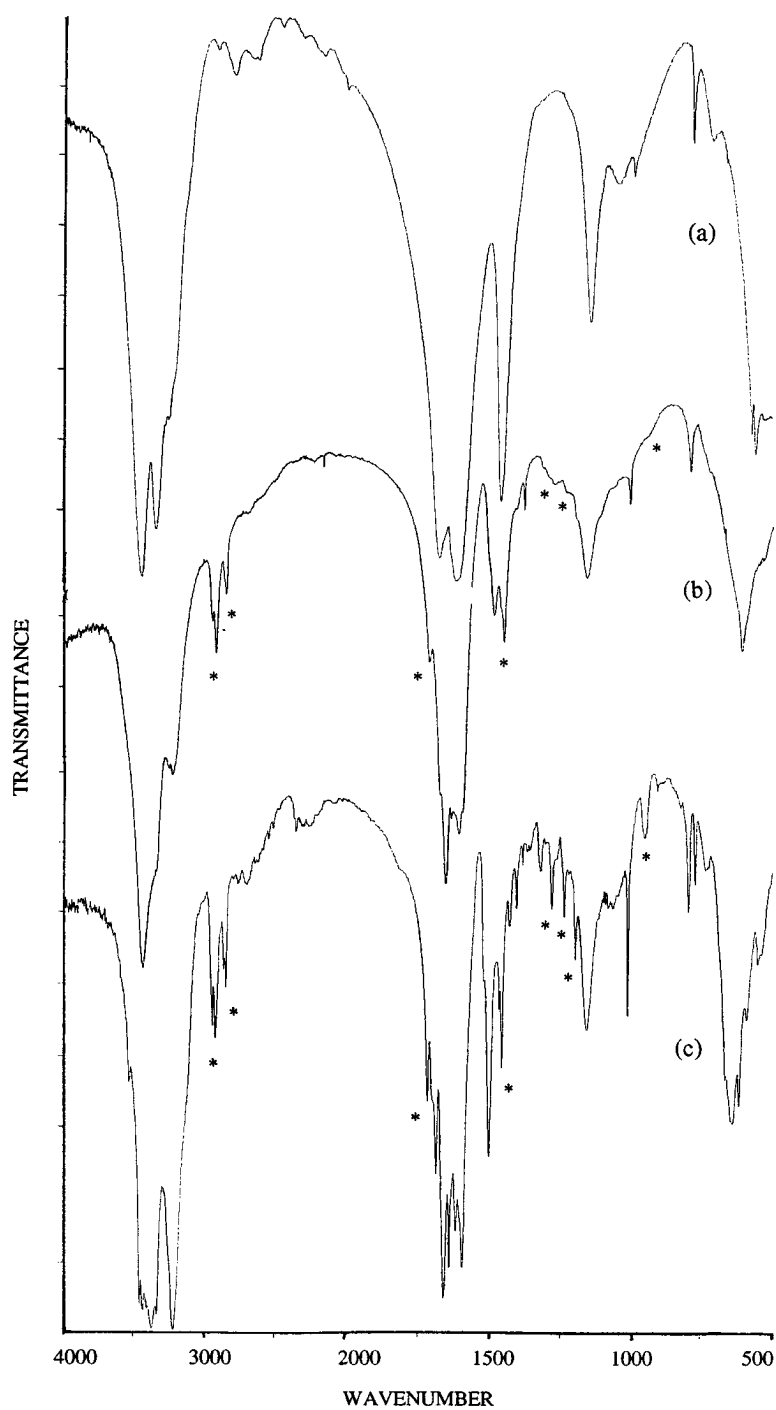


Figure 2. The IR spectra ($4000\text{--}500\text{ cm}^{-1}$) of (a) tetragonal urea and of the octanoic acid inclusion compound at RT (b) and at 93 K (c). Guest bands marked *.

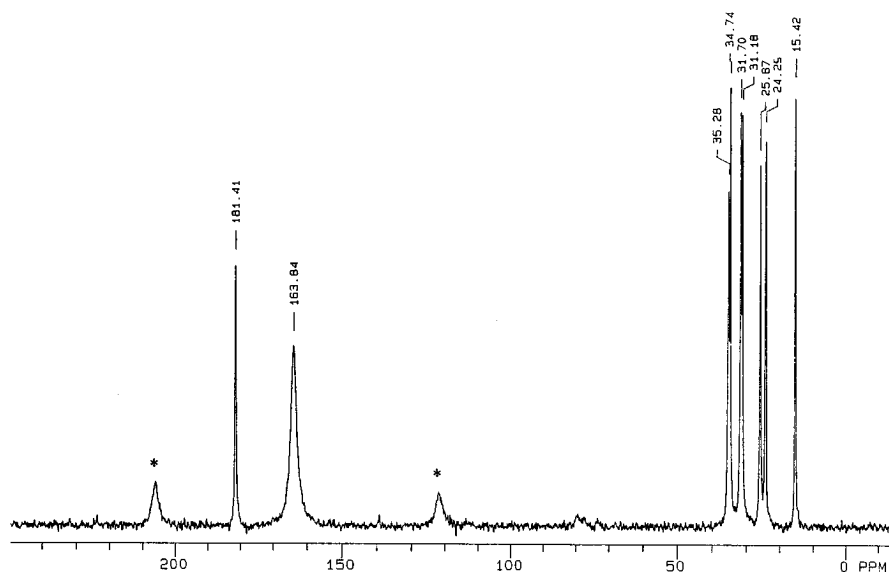


Figure 3. ^{13}C MASNMR spectrum of the urea/octanoic acid inclusion compound. The peak at 163.8 ppm is due to the urea host. Spinning side bands marked *.

chemical shift values of acids from butyric onwards were lower than the liquid phase shifts by values ranging from 9.5 ppm (butyric acid) to 3.8 ppm (octanoic acid). The guest acids in Dianin's compound are present as monomers in the cavity with a *host-guest* interaction rather than the *guest-guest* interaction present in the urea inclusion compounds.

3.3.2. Guest Alkyl Resonances

The Δ values ($\delta_{\text{guest}} - \delta_{\text{solution}}$) for the guest alkyl resonances (Table III) are all positive, apart from the 2 exceptions for the CH_3 resonances of valeric (-0.5) and heptanoic (-0.2) acid. This is very different from the Δ values of the acids as guests in Dianin's compound [1] where many negative values were observed. The largest negative values were observed for the CH_3CH_2 resonances of the heptanoic (-1.7) and octanoic (-2.7) acid guests. These upfield shifts were attributed to the *gauche* conformation of the methyl group as deduced from the crystallographic study [10]. Alcohol [1] and alkane [11] guests display a similar behaviour. These conformations are required in order for the guest acids to fit into the restricted space available in the *cavity* formed in the Dianin host lattice.

The *channel* like voids available in the urea host lattice should not affect the end conformation of the molecule. *n*-Alkanes and 1-substituted long chain alkanes as guests have long been considered to have the all-*trans* conformation [2]. MM calculations on alkane inclusion compounds have however indicated that, whilst the all-*trans* conformation is the most abundant, other conformations are possible

Table III. ^{13}C chemical shift values, relative to TMS, for the guest resonances.

Guest	C=O	Alkyl chain
<i>n</i> -Butyric acid	181.4 (179.7, 181.0)	14.3, 19.5, 37.1 (13.5, 17.9, 35.7)
Δ	0.4	0.8, 1.6, 1.4
<i>n</i> -Valeric acid	181.5 (179.8, 180.9)	13.1, 23.1, 26.8, 34.4 (13.6, 22.0, 26.5, 33.6)
Δ	0.6	-0.5, 1.1, 0.3, 0.8
<i>n</i> -Hexanoic acid	181.6 (179.8, 180.9)	15.4, 23.8, 26.1, 33.6, 35.0 (13.8, 22.1, 24.1, 31.1, 33.8)
Δ	0.7	1.6, 1.7, 2.0, 2.5, 1.2
<i>n</i> -Heptanoic acid	181.3 (179.8, 180.8)	13.7, 24.3, 25.8, 31.2, 32.1, 35.5 (13.9, 22.3, 24.3, 28.6, 31.3, 33.9)
Δ	0.5	-0.2, 1.0, 1.5, 2.6, 0.8, 1.6
<i>n</i> -Octanoic acid	181.4 (179.8, 180.7)	15.4, 24.3, 25.9, 31.2, 31.7, 34.7, 35.3 (13.9, 22.4, 24.4, 28.8, 28.9, 31.5, 33.8)
Δ	0.7	1.5, 1.9, 1.5, 2.4, 2.8, 3.2, 1.5
<i>n</i> -Nonanoic acid	181.2 (179.9, 180.7)	14.1, 24.6, 25.5, 31.3, 32.7 ^a , 35.7 (13.9, 22.4, 24.4, 28.9 ^b , 29.1, 31.6, 33.9)
Δ	0.5	0.2, 2.2, 1.1, 2.4, 3.8, 3.6, 1.1, 1.8)
<i>n</i> -Decanoic acid	181.3 (179.8, 180.5)	14.9 [*] /15.3, 24.5/25.0 [*] , 25.7, 31.3, 31.6, 32.3, 32.9/33.5 [*] , 34.5 [*] /34.9, 35.5 (14.0, 22.9, 24.7, 28.9, 29.1, 29.2, 31.7, 33.9)
Δ	0.8	1.3, 1.6, 1.0, 2.4, 2.5, 3.2, 3.7, 3.2, 1.6

Values in parentheses: C=O shift – 5% solution in CCl_4 and the neat liquid respectively.
Alkyl chain shifts – 5% solution in CCl_4 .

Δ values: C=O values: guest-liquid values: alkyl chain values: guest-solution values for decanoic acid.

Δ value given is for the stronger component.

^a Triply degenerate.

^b Doubly degenerate.

* vw component.

[12]. The ^{13}C chemical shift values of the acid alkyl chains resemble the shifts of guest alkanes in having positive Δ values [13], indicating that the alkyl chains have conformations similar to those of the alkane chains. Some of the bands of the decanoic acid guest are accompanied by weaker components (Table III). By comparison with the MM studies on alkane guests these weak bands are tentatively assigned to small populations of conformations other than all-trans.

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