

Synthesis and Structural Aspects of Urea/Dialkylamine Inclusion Compounds

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Abstract. The synthesis and structural aspects of urea host-guest inclusion compounds containing linear secondary alkylamines (dibutyl-, dipentyl-, dihexyl-, dioctyl-) at 25 °C are reported. Elemental analysis, ¹³C CP-MAS NMR and ¹H-NMR Spectroscopy, and Powder X-ray Diffraction Analysis confirm the inclusion process. The basic host structure of the products is similar to that of urea-hydrocarbon systems. ¹³C MAS-NMR experiments show chemical shift differences for the confined guest molecule with respect to the liquid phase. Stoichiometry and $|c_g|$ values for the inclusion compounds with dipentyl- and dihexylamine suggest a commensurate structure.

Key words. Inclusion compounds, urea clathrates, dialkylamine inclusion.

1. Introduction

Urea, which is known to form crystalline inclusion compounds in the presence of appropriate organic molecules, is a host species of special interest because of its potential for modeling cavities formed by peptides in biological systems. Such kinds of compounds may be described as extensively hydrogen bonded urea host structures with linear, parallel, infinite hexagonal channels where the guest molecules are located [1–5], Figure 1.

Urea forms inclusion compounds not only with hydrocarbons and their halogenated derivatives, which are in general rather inert substances, but also with other chemical species with carboxylic, alcohol, ester [1, 4–7], cyano [8] and amine [9] functional groups which are potentially more active in the formation of hydrogen bonding with the urea. In most cases the included species appear to be loosely located in interstitial spaces and no specific host-guest interactions are detected. Recently it has been reported however that in the special case of 1,8-dicyanooctane (sebaconitrile) a distortion of the urea channels, caused apparently by host-guest hydrogen bonding interactions, is observed [8]. The relatively broad NMR signals, as well as the chemical shifts of the nitrile, agree with the commensurate nature of the nitrile in that clathrate. Is that a single case or is it the result of the concurrence that in general should occur between urea–urea and urea–guest interactions?

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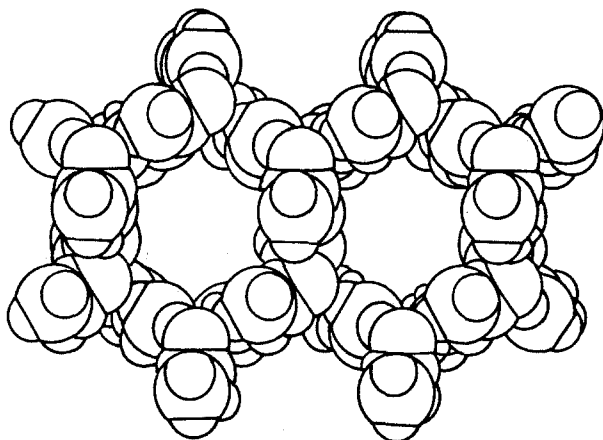
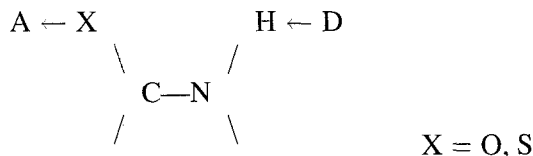


Fig. 1. Representation of the basic host structure in urea inclusion compounds viewed along the channel axis using the conventional van der Waals radii.

What Lewis basicity of the guest is necessary to distort or to disrupt the clathrate urea structure? Is the guest basicity the main factor in this kind of molecular recognition? We think that in order to answer these questions further knowledge about the ability of urea for including species with other functional groups is required.

Amidic compounds interact with Lewis acids and bases via the formation of hydrogen bonds or by classical coordinative interactions:



For a given compound, the strength of the interaction will be mainly determined by the donor and acceptor capacity of A and D respectively [10, 11]. Considering the Donor Number as a measure of the donor strength of Lewis bases, the basicity of amines is in general considerably higher than that of oxygen donors such as alcohols, ethers, amides and sulfoxides. Aliphatic amines could therefore compete for hydrogen bonding with the urea affecting the formation of the host structure. In order to investigate the effect of such a competition the formation of inclusion compounds with a series of secondary alkylamines was investigated.

Experimental

Commercially available reagents were used as received. The products were obtained from solutions of both amine and urea in methanol by slow solvent evaporation at

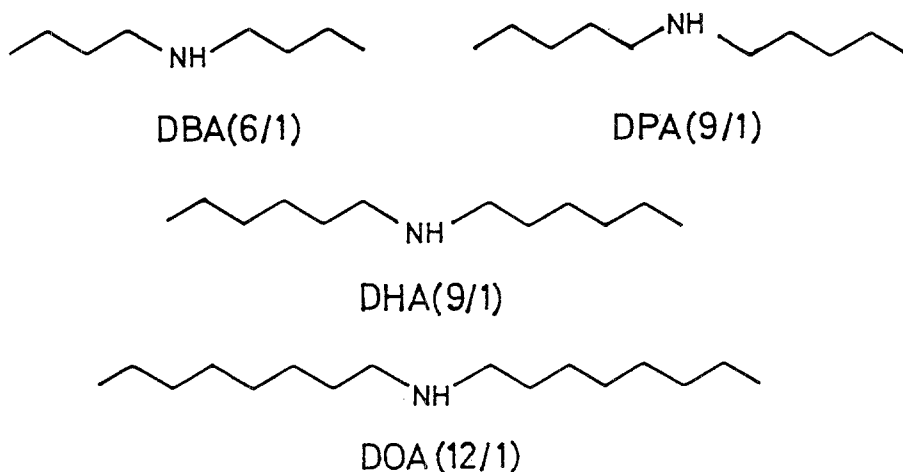


Fig. 2. Guest species in the different inclusion compounds discussed in this paper and urea/amine ratio. DBA = dibutylamine, DPA = dipentylamine, DHA = dihexylamine, DOA = dioctylamine.

room temperature. Amine to urea molar ratios used in the experiments were always somewhat greater than those expected for the products. Crystals with well formed faces were separated after about 48 h, washed with cold methanol and dried under vacuum. Urea:amine ratios reported in Figure 2 were determined by both elemental microanalysis (Perkin Elmer 240C microanalyzer) and dimethyl- d_6 sulfoxide solutions ^1H -NMR spectroscopy. Products were further characterized by optical microscopy inspection, X-ray diffraction analysis of microcrystalline samples, and NMR spectroscopy.

^1H and ^{13}C high resolution solution NMR spectra were recorded on a Bruker AMX-300. The ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectra were recorded on a Bruker MSL-100 spectrometer at a frequency of 100.63 MHz for ^{13}C . The numbers of scans varied between 200 and 1200 with $5.5 \mu\text{s}$ 90° pulses, 1 ms cross-polarization contact time, 41 ms acquisition time during proton decoupling and 5 s recycle delay. The polycrystalline powder samples were spun at a frequency of 4 kHz using a Bruker CP-MAS probe. The chemical shifts are given relative to tetramethylsilane (TMS), determined *via* the use of internal standard. Powder X-ray diffractograms were recorded in the range $2^\circ > 2\theta > 50^\circ$ on a Siemens D-5000 diffractometer using $\text{CuK}\alpha$ radiation (40 KV, 30 mA) and a graphite monochromator ($\lambda = 1.5418 \text{ \AA}$). Samples were ground to a fine powder in order to reduce the likelihood of the crystallites exhibiting a preferred orientation. For all the products apart from dibutylamine-(6 urea), DBA-(6 urea), the diffractograms indicate the absence of any other crystalline phases other than those of the reported inclusion compounds. The diffractograms reveal that in addition to the peaks corresponding to the host structure some peaks corresponding to guest reflections may be identified: $2\theta = 5.431^\circ(001)_g$ and $13.540^\circ(101)_g$ for dipentylamine-(9

TABLE I. Lattice parameters of the hexagonal space group $P6_122$ structure at room temperature.

Urea inclusion compound	$ a_h $ (Å)	$ b_h $ (Å)	$ c_h $ (Å)
DPA-(9 urea)	8.244 (9)	8.244 (9)	11.010 (9)
DHA-(9 urea)	8.227 (2)	8.227 (2)	11.032 (5)
DOA-(12 urea)	8.230 (3)	8.230 (3)	11.041 (8)

DPA = dipentylamine, DHA = dihexylamine, DOA = dioctylamine.

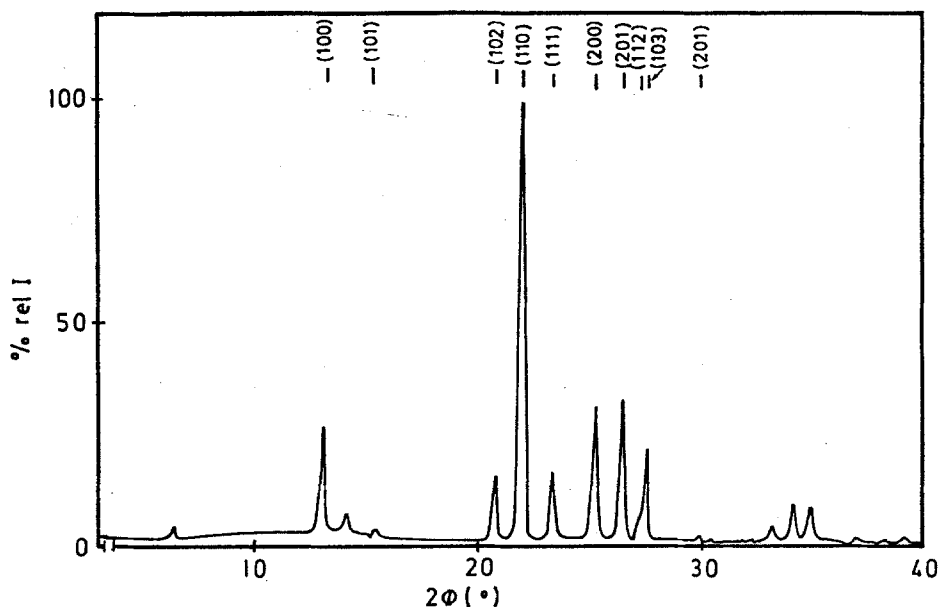


Fig. 3. Indexed powder X-ray diffractogram for the matrix in DPA-(9 urea) inclusion compound at 296 K ($\text{CuK}\alpha$ radiation).

urea), DPA-(9 urea); $2\theta = 4.767^\circ(001)_g$ and $13.540^\circ(101)_g$ for dihexylamine-(9 urea), DHA-(9 urea); and $2\theta = 3.917^\circ(001)_g$ and $12.979^\circ(101)_g$ for dioctylamine-(12 urea), DOA-(12 urea). The DBA-(6 urea) diffractogram exhibits principally the pattern corresponding to the urea tetragonal phase [2, 12].

Results and Discussion

Analytical as well as further characterization of the products clearly show that secondary amines $\text{CH}_3(\text{CH}_2)_n\text{NH}(\text{CH}_2)_n\text{CH}_3$ with $n = 3, 4, 5,$ and 7 , can be accommodated by urea matrices to form stable inclusion compounds which are similar to those obtained from the inclusion of hydrocarbons $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ with $n > 4$ in the same host at 25°C [13]. Experimental evidence for such compounds may be obtained by considering two sublattices, namely those corresponding to

TABLE II. Information relating to the guest in dialkylamine/urea inclusion compound.

Urea inclusion compound	Guest length (Å)	$ c_g $ (Å)	$ c_g / c_h $
DBA-(6 urea)	11.724	—	—
DPA-(9 urea)	14.239	16.262	1.477
DHA-(9 urea)	16.754	18.521	1.679
DCA-(12 urea)	21.783	22.546	2.041

See abbreviations in Table I.

TABLE III. Chemical shifts of dipentylamine inserted in the urea matrix compared with those of the amine in other media.

Assignment	Guest in urea matrix	Guest in CCl ₄ (10% v/v)
C _α -1(1)	52.58	49.51
C-2(2)	32.65	29.62
C3(3)	31.17	29.15
C4(4)	24.51	22.13
C5(5)	14.58	13.23

both the host, characterized by the parameters $|a_h|$, $|b_h|$, $|c_h|$, and the guest with the parameters $|a_g|$, $|b_g|$, $|c_g|$ [4]. The lattice parameters of the host sublattice obtained mainly from X-ray analysis of polycrystalline samples of the products at room temperature are reported in Table I. Indeed most of the peaks in the diffractograms, independently of the included amine, can be indexed on the basis of a hexagonal lattice with parameter values close to $|a_h| = |b_h| \approx 8.2 \text{ \AA}$, $|c_h| \approx 11.0 \text{ \AA}$, $\alpha_h = \beta_h = 90^\circ$ and $\gamma_h = 120^\circ$. A typical indexed diffractogram, that for the compound DPA-(9 urea), is shown in Figure 3. Moreover, these features correspond to a two dimensional array of hexagonal channels along which the translation repeat unit (c) of about 11 \AA is always the same, independent of the size of the guest, agreeing therefore with the basic host structure observed for urea–hydrocarbon inclusion compounds [6]. Crystal inspection by optical polarizing microscopy ratify the assignment to a hexagonal crystal system. In all cases, hexagonal prismatic crystals which can be readily distinguished from those of the urea crystallizing as tetragonal prisms are observed. The crystals appear as almost perfect regular hexagons, contrasting with those of the urea–hydrocarbon inclusion compounds for which distorted hexagons are usually observed [4].

Information about the sublattice amine is much more difficult to obtain. From the amine–urea stoichiometric ratios, which in all cases satisfy the relationship $1:3n$ ($n = 2, 3$ or 4) it follows that an amine guest molecule, depending on its molecular length, must occupy either 1, 1.5, or 2 channel repeat units. This feature points to a commensurate structure. The space periodicity of the guest species

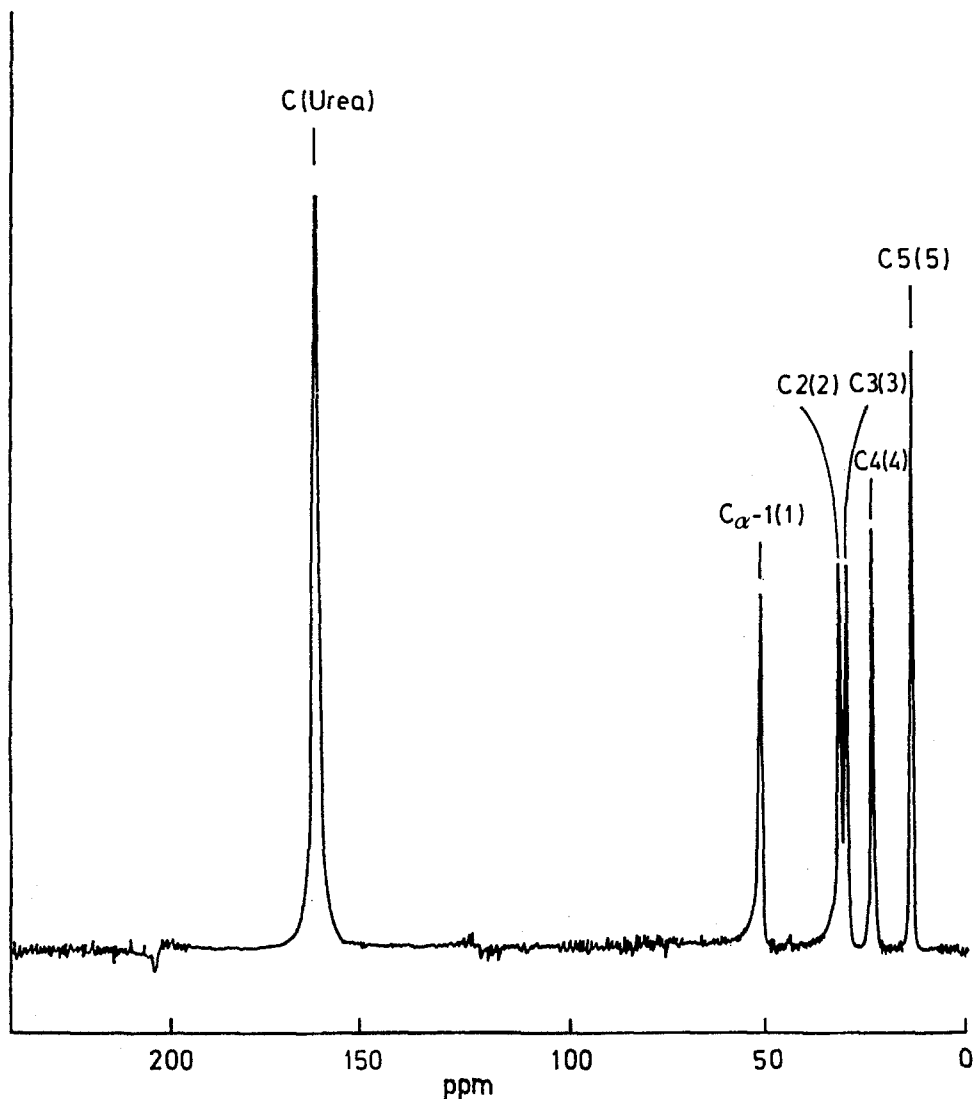


Fig. 4. ^{13}C CP-MAS NMR spectrum of the DPA-(9 urea) at room temperature and at 100.63 MHz. The urea/dialkylamine inclusion compounds have a resonance at about 163.3 ppm due to the carbon in the urea molecule.

$(|c_g|)$ along the channels, which due to the good quality of the diffractograms could be unequivocally obtained for three of the studied compounds (*vide supra*), are comparable to the length of the guest molecule in its most extended linear conformation [4]. Moreover, as observed in Table II, which compares the $|c_g|$ values obtained with the lengths of the guest molecules, the $|c_g|$ values are almost multiples of $1/2 |c_h|$. These features concur with a commensurate structure in which

the amine is confined in the urea channel occupying a space formed by an entire multiple of chemically equivalent units (3 urea molecules with a length of ca. 5.5 Å) which is one half of the crystallographic repeat unit.

Further information about the state of the guest has been obtained from the NMR spectra of the products. The ^{13}C CP-MAS NMR spectra of the solids at room temperature show a pattern which is similar to those of the same amine as a pure liquid or dissolved in carbon tetrachloride. High-amplitude motions of the amine guest molecules in the channel average the residual dipolar interactions between ^{13}C and ^{14}N to less than 25 Hz. ^{13}C - ^{14}N residual dipolar interaction is not averaged to zero by MAS. The axis of quantization of the ^{14}N nucleus is tilted from the direction of the static magnetic field as a consequence of the interaction between the ^{14}N nuclear quadrupole moment and the electric field gradient at the ^{14}N nucleus [8,14]. In Table III are reported the chemical shifts of dipentylamine inserted in the urea matrix with those of the amine in other media. Figure 4 reproduces the ^{13}C CP-MAS NMR spectrum of DPA-(9 urea).

The behavior of organic molecules placed in environments such as those occurring within clathrate cavities is expected, in general, to differ from those of the same molecule in other phases [15–17]. In this work, the ^{13}C -NMR behavior of the dipentylamine was analyzed in some detail. Indeed, the effect of the amine autoassociation on the chemical shifts can be appreciated by observing the shifts on going from the pure liquid to a dilute solution in CCl_4 . Interestingly, the ^{13}C -chemical shifts of the dipentylamine inserted in the urea correspond to the free amine or at least to an amine undergoing weaker interaction with the medium than the amine dissolved in an inert solvent. Urea channels appear to be, concerning these secondary amines, a perfect van der Waals cavity.

From the results discussed above it can be then concluded that urea, in the presence of species fulfilling some specific size and shape requirements, forms normal commensurate inclusion compounds accommodating the guests in hexagonal channels in spite of the basicity of the included species.

Acknowledgments

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