

Structural studies of urea clathrates with long aliphatic amines

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Although urea is a relatively small molecule, it forms many unusual structures, such as clathrates. The first urea clathrate structures were identified in the 1980s. It was shown that urea molecules, interacting through hydrogen bonds, form hexagonal channels that can accommodate guest molecules. These channels are infinite, allowing guest species a certain degree of mobility within them, which in turn leads to positional disorder. Studies on clathrates have shown that systems that can be incorporated into urea channels include unbranched aliphatic hydrocarbon molecules and their derivatives [1-3]. In 2002, finite urea channels were obtained, closed at both ends by solvent molecules [4].

Our studies of these systems have led to the formation of clathrates with long-chain aliphatic amines: undecylamine (N11), dodecylamine (N12), tetradecylamine (N14), hexadecylamine (N16), and octadecylamine (N18). Methanol is also incorporated into the crystal lattice of each of these structures. Within each channel, two amine molecules are oriented with the amine groups outward, which allows interaction with the methanol molecule. This arrangement leads to the formation of a closed channel structure and results in relatively ordered guest molecules. It is worth noting that the cross-section of these channels does not resemble a perfect hexagon, as is the case for infinite urea clathrates. The N11, N12, and N14 systems crystallize in the $C2/c$ space group, N16 in $P2_1/c$, whereas N18 in $P2_1/n$. In the asymmetric part of N11, N12 and N14 structures, one amine–methanol pair is present alongside to urea molecules. Undecylamine and dodecylamine molecules occupy two alternative positions. In clathrates N16 and N18, two amine–methanol pairs are present and no disorder is observed in these systems. The channels formed in all obtained structures are chiral.

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