Poster

Structural studies of urea clathrates with aliphatic monoamines

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Urea, the first naturally occurring compound synthesized by F. Wöhler nearly 200 years ago, continues to attract considerable interest [1]. Its derivatives find applications in various fields, ranging from cosmetology [2] to the production of explosives [3]. Due to its low toxicity and wide availability, urea is widely utilized in organic synthesis. The ability of urea molecules to form hydrogen bonds enables the creation of intricate three-dimensional supramolecular structures. These structures include both macrocyclic molecules and clathrates, which are crystal systems with channel-like structures that encapsulate guest molecules within urea frameworks.

Urea clathrates, initially discovered in the 1940s, have received relatively limited attention in research [4]. Among the most prevalent clathrate arrangements are those forming infinite channels resembling honeycombs, capable to accommodate linear-shaped guest molecules that typically remain in a disordered state. Importantly, urea can also form clathrates with channels of varying lengths, depending on the guest molecule. Such systems are often sealed by a small molecule, and the guest molecule itself exhibits high order within the channel structure.

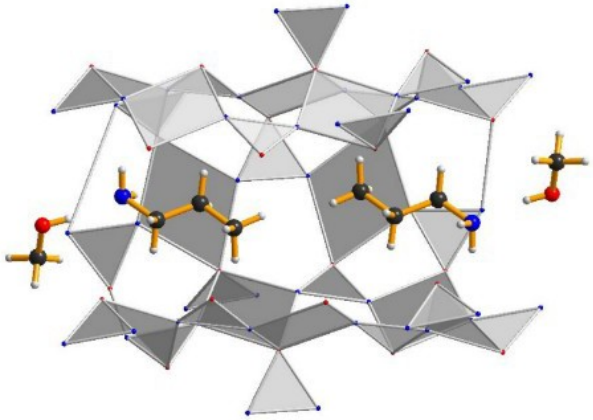

Figure 1. Urea clathrate with 1-aminopropane.

The current study focuses on the structural analysis of finite urea clathrates formed with aliphatic monoamines. A total of eight structures were obtained using a series of successive amines from 1-aminopropane to 1-aminodecane. Given the high volatility of low molecular weight amines, these compounds exhibit relatively low stability, therefore research need to be conducted at low temperatures. In all obtained systems, two amine molecules are present within the urea channel, with their hydrophobic tails oriented towards the interior. A hydrophilic amino group extends from the channel and forms a hydrogen bond with the closing molecule, methanol. Notably, a significant correlation between the length of the amine chain, represented by the number of carbon atoms, and the lattice constant ***c*** is observed. Most of the studied systems crystallize in the *C2/c* space group, except for the clathrates with 1-aminopropane and 1-aminoheptane, which belong to the $P2_1/c$ group. This distinction is most likely due to the adjustment of the clathrate tube length to the size of the guest molecule. The binding energy of the urea molecule within the channel was found to be approximately at the level of -30 kcal/mol.

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[2] D. Voegeli, *Derm. in Practice*,**18** (2012) 13

[3] R. Matyas , J. Selesovsky, V. Pelikan, et. al., Explosive Properties and Thermal Stability of Urea Hydrogen Peroxide Adduct, Propellants, Explosives, Pyrotechnics, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, (2016)

[4] M. F. Bengen, *Angew. Chem*., **6** (1951) 207