



	Experiment title: Host-guest hydrogen bonding in high-pressure clathrates	Experiment number: CH-6293
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Report:

The goal of this proposal was to investigate clathrates of tetrahydrofuran and 1) to illuminate their high-pressure-low-temperature polymorphism with usage of *in situ* X-ray diffraction and 2) understand how addition of methanol in the system affects the crystallisation pathway.

For this purpose, two solutions have been prepared: tetrahydrofuran (THF)-H₂O (1:3, **Experiment 1**) and THF-methanol (Mt)-H₂O (0.5:0.5:3, **Experiment 2**). Membrane-driven Le Toullec-type diamond anvil cells with culet diameter of 700 μm were used for pressure generation. The sample chambers with the approximate diameter of 400 μm were obtained by drilling stainless steel gaskets preindented to 80 μm. The solutions were loaded in the sample chambers along with rubies for pressure estimation and then pressurised to 0.3-0.4 GPa before placing into cryostat. The solutions were investigated in the range 0-1.7 GPa and 200-300 K. Powder and single-crystal X-ray diffraction has been performed on the solid phases wherether formed. The results of the experiments are summarised in the Figure 1.

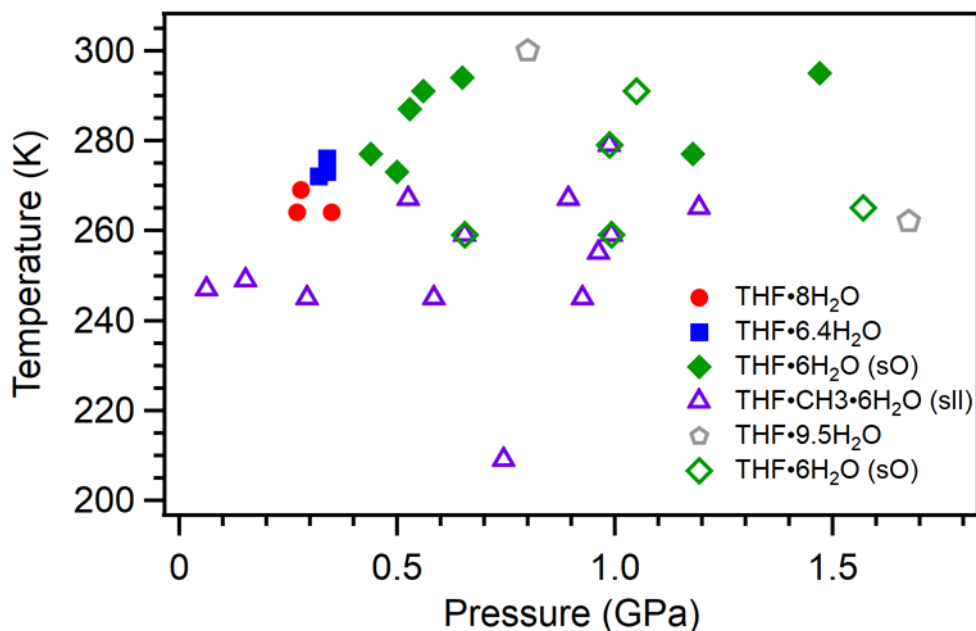


Figure 1. Pressure–temperature phase diagram indicating the conditions at which diffraction data for THF clathrates were collected in the present study.

In **Experiment 1**, in the THF-H₂O System, three solid phases have been observed. Firstly, upon cooling of the pressurized solution, a clathrate hydrate crystallized in hexagonal symmetry, with space group $P6_3/mmc$, and unit cell dimensions $a = 12.3979(8)$, $c = 24.661(10)$ Å (at 0.27 GPa and 264 K). The structural refinement produced nearly the same framework topology as described previously for the isopropylamine (IPA) octahydrate, $10(\text{CH}_3)_2\text{CHNH}_2 \cdot 80\text{H}_2\text{O}$ (McMullan et al. 1970). Upon slight heating, the THF octahydrate has transformed. New phase crystallized in hexagonal symmetry, with space group $P6_3/mmc$, and unit cell dimensions $a = 12.644(4)$, $b = 11.1417(8)$, and $c = 6.5280(3)$ Å (at 0.32 GPa and 272 K). The structural refinement resulted in a framework topology that was recently described for 6 3/7 cyclobutylamine (cBA) hydrate (Dobrzycki et al. 2016). Upon pressure increase, occurrence of another phase has been observed. The new phase crystallized in orthorhombic symmetry, with space group $P2_12_12_1$ and unit cell dimensions $a = 12.6149(10)$, $b = 11.5016(6)$, and $c = 6.6353(2)$ Å (at 1.05 GPa and 282 K, SI), indicating that the sO structure was formed that was previously described for THF (Kurnosov et al. 2004) and acetone (Manakov et al. 2007; Pakhomova et al. 2022) clathrate hexahydrates. The sO THF clathrate was found to be stable up to the highest studied pressure of 1.4 GPa.

Addition of methanol (Mt) into in the THF-H₂O system dramatically changed the P-T induced transformation pathway. Upon cooling of the pressurised solution THF-Mt-H₂O in the **Experiment 2**, the common cubic sII clathrate, with space group $Fd-3m$ and unit cell dimension $a = 12.644(4)$ Å has crystallised at 0.15 GPa and 249 K. Strikingly, the sII clathrate persisted up to 1.2 GPa at least. After pressure increase to 1.67 GPa at 265 K, the sII underwent transformation to a new phase with space group $P6/mmm$ and unit cell dimensions $a = 11.8229(9)$, and $c = 11.949(4)$ Å (at 1.67 GPa and 265 K). The structural refinement resulted in a framework topology that was recently described for 9.5-cyclobutylamine (cBA) hydrate (Dobrzycki et al. 2016). Right after the data collection, the sample has transformed to the sO phase, previously also observed in this study for the binary THF-H₂O system. Upon heating and decompression of the sO clathrate, the sII clathrate was recovered again at 0.99 GPa and 279 K. sII and sO were found to be coexisting (SI photo) upon decompression down to 0.65 GPa and cooling down to 259 K. Then upon T increase to 267 K the sO phase has disappeared. The sII phase remained stable upon cooling down to 209 K.

The comparison of behavior of binary THF-H₂O and ternary THF-H₂O-Mt systems at low temperatures and high pressures allows us to demonstrate the unexpected role of methanol on the crystallization pathway. While it acts as an antifreeze and lowers the melting curve (Figure 1) as discussed in the previous studies, methanol also acts as a guest molecule occupying a small cage of sII clathrate. Likely, presense of Mt in the cages is responsible for striking and unexpected persistence of sII structure above 1 GPa.