

# **$\beta$ -hydroquinone clathrates: Insight into host-guest chemistry**

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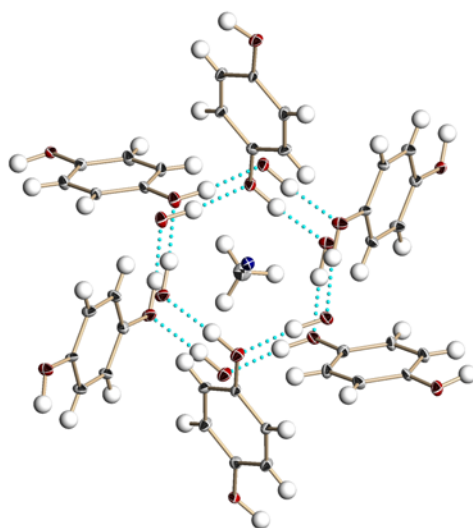
Supramolecular chemistry is the foundation of design and development of materials with a vast number of potential applications such as catalysis, targeted drug delivery and gas storage. This research is part of a project that aims to make a novel contribution to understanding of intermolecular interactions, with special focus on crystalline guest-host systems as the  $\beta$ -hydroquinone clathrates,  $3\text{C}_6\text{H}_4(\text{OH})_2 \cdot x\text{S}$  with S being the enclathrated solvent [1].

Analysis of an experimentally determined charge distribution of the organic clathrates provides information such as the electrostatic properties of the host lattice as well as the guest molecules, from which an estimation of the formation energies can be given. In high accuracy studies unbiased structural parameters (e.g. thermal and positional) will be obtained from neutron single crystal diffraction.

Using synchrotron X-ray radiation, the data of three different  $\beta$ -hydroquinone clathrates were collected at the D3 beamline at the German Electron Synchrotron DESY. A large amount of diffraction data were obtained using a Huber 4-circle diffractometer with a Mar165 CCD area detector in combination with He-cooling to 15(2) K and a wavelength of 0.477(1) Å (~26 KeV). The structures of the clathrates crystallize in the hexagonal space groups P3, R3 or R-3.

The host structure has the pseudo symmetry R-3, but the positioning of the solvent molecules can lower the symmetry to R3 or P3. The framework is built up of hydrogen-bonded quinol molecules arranged so as to enclose the guest molecules, but without generating any chemical link between the framework and the enclathrated guest molecule, see Figure 1. The occupation can range from empty void to a fully occupied void depending on enclathrated solvent and synthesis route. In a fully occupied clathrate the ratio between host hydroquinone and guest solvent is 3:1.

Refinement using an independent atom model has been successful for the  $\beta$ -hydroquinone clathrates with solvents  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{NC}$ , but so far multipole refinements have failed. The topological analysis of the density suggests that there is no direct bonding between neighbouring Co atoms, which is explained by theoretical calculations on a single molecule by the observation that the complex is in a singlet di-radical state. Furthermore, much to our surprise it was not possible to locate all Co-C bond critical points to the bridging alkyne, which is speculated to result from the random noise of the observations or the effect of the crystal field, or perhaps the flexibility of the model is too small, or perhaps a combination of these effects.



**Figure 1:** One enclathrated acetonitrile molecule in the void of the hydroquinone host framework. Only the hydroxyl groups of the hydroquinone molecules above and below the void have been shown for clarity. Thermal ellipsoid probability is at 90%.

## References

- [1] G. R. Desiraju, *Comprehensive Supramolecular Chemistry*, Vol. 6, 1 (1996)