

**Experiment title:****Diffuse scattering in a tunable clathrate****Experiment****number:**

01-02-635

Beamline:

BM01A

Date of experiment:

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Shifts:

6

Local contact(s):

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Report:

Background: When the host trans-9,10-dihydroxy-9,10-bis(p-tert-butyl-phenyl)-9,10-dihydroanthracene (H) is exposed to mixtures of dimethylformamide, A, and dimethylsulfoxide, B, it forms an usual series of five distinct inclusion compounds: H.4A, H.3A.B, H.2A.2B, H.A.3B and H.4B. Their crystal structures are triclinic with similar cell dimensions and P-1 space group symmetry [1,2]. There is one centrosymmetric host and two pairs of centrosymmetrically related guest molecules per unit cell. The five compounds are isostructural with respect to the location of the host molecules. For the compound H.3A.B, symmetry requires that on average the guest B and one of the guests A be located on the same site each with half occupancy (Figure 1). Such disorder in combination with the stoichiometric composition of the inclusion compounds raises the question whether the structure is to be described as a 1:1 mixture of H.4A and H.2A.2B unit cells, a disordered arrangement of H.3A.B unit cells or both. In order to elucidate the nature of the disorder a diffraction experiment using synchrotron radiation was carried out on H.3A.B and H.2A.2B compounds, the latter serving as reference.

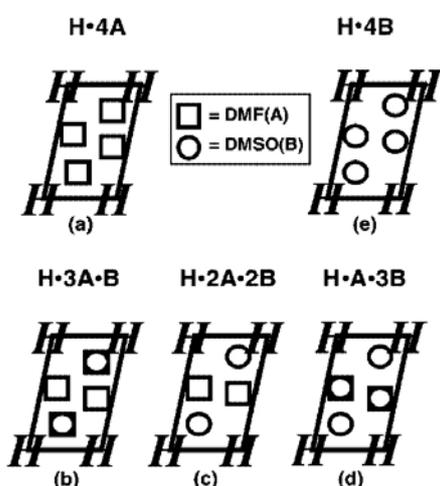


Figure 1. Schematic diagram summarising the differences between the five host-guest structures. The host molecules are symbolized by *H*, while the solvent guest molecules are represented by squares (A) and circles (B). Note the co-existence of squares and circles on the same site for the H.3A.B and H.A.3B compounds.

Experimental procedure and Results:

(i) Bragg-data sets were collected on H.3A.B and H.2A.2B samples, at 120 K with $\lambda = 0.700(1)$ Å, the MAR detector and 2° oscillation per image, in order to allow an accurate refinement of their average crystal structure. The results of the refinement of the average crystal structures are $R_{\text{int}} = 0.037$, $R_1 = 0.043$, $wR_2 = 0.113$ and $S = 1.024$ for the reference compound H.2A.2B, and $R_{\text{int}} = 0.042$, $R_1 = 0.085$, $wR_2 = 0.277$ and $S = 1.050$ for compound H.3A.B. These results are better in terms of confidence factors than those reported for sealed-tube data [1], $R_1 = 0.097$ and $R_1 = 0.141$, respectively.

(ii) Diffuse scattering data were measured at the same temperature with a finer slicing, 0.6° oscillation per image. Reciprocal sections were reconstructed from the raw images (fig. 2). The interpretation of these data is underway. Based on the average structure of H.3A.B, the regions of the reciprocal space that are relevant for the scattering of the following quadruples of guest molecules 4A, 3A.B and 2A.2B will be identified. Comparison with the observed diffuse features should allow to identify which type of pair predominates. The quantitative interpretation will make use of the genetic algorithm previously used to analyse the diffuse scattering observed for another inclusion compound [3].

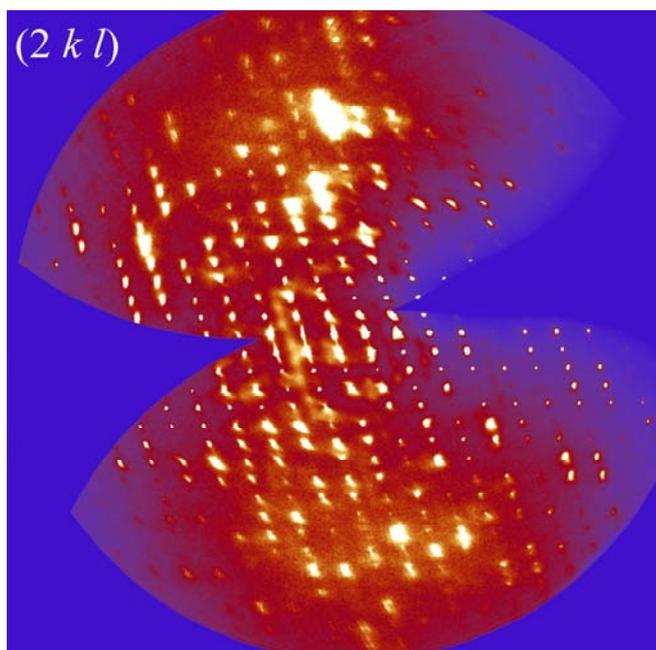


Figure 2. (2 k l) reciprocal layer of compound H.3A.B reconstructed from the data collected at BM01A at the ESRF (MAR345 detector, 0.6° slicing, 120 K)

References

- [1] M. R. Caira, T. le Roex, L. R. Nassimbeni, *Chem. Commun.*, 2001, 2128-2129;
- [2] L.J. Barbour, M.R. Caira, T. le Roex, L.R. Nassimbeni, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1973-1979.
- [3] Th. Weber, H.-B. Bürgi, *Acta Cryst. A***58**, 2002, 526-540.