Experimental report

15/08/2016

Proposal: 5-12-318 **Council:** 4/2015

Title: Distortions in urea inclusion compounds

Research area: Chemistry

This proposal is a new proposal

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Samples: Urea-octanedione
Urea.DMF

Instrument	Requested days	Allocated days	From	To
D19	14	7	15/09/2015	23/09/2015

Abstract:

We have obtained precise neutron structures of hexagonal and 'slightly' distorted urea channel inclusion compounds. We now propose to undertake neutron structure determination of a highly distorted channel inclusion complex of octane dione which exhibits explicit urea-guest hydrogen bonding that is linked to the ferroelastic behaviour of these materials. We also propose to structurally characterise the urea-dimethylformamide inclusion complex in which the hexagonal channel structure has partially broken down due to explicit guest-urea hydrogen bonding interactions.

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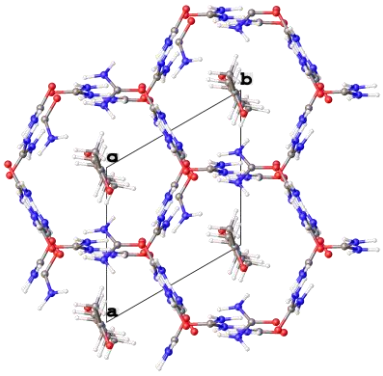
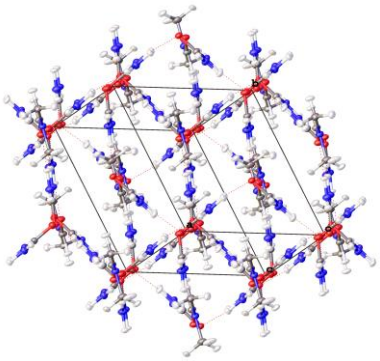
Single crystal neutron structures at several temperatures have been determined for a β-phase urea inclusion compound containing 2,7-octanedione. The neutron structure of the 'partial channel' co-crystal of urea and DMF was also obtained. Data were collected to facilitate an in-depth discussion and analysis of the structure and bonding of a urea series, including urea inclusion compounds of *n*-hexadecane and 1,6-dibromohexane, previously studied at ILL (see experimental report for 5-12-308).

Experimental

Neutron diffraction data were collected using instrument D19 on crystals of urea/2,7-octanedione (OCT) and urea/dimethylformamide (UDM). Initially data were collected on UDM at a wavelength of 1.1698 Å at 30 and 120 K. For OCT, a wavelength of 1.4547 Å at 30 K was used due to an unusually long *c* axis of 76 Å. An analytical crystal absorption correction and vanadium can absorption correction were applied to each data set. Structure solution and refinement were carried out using the SHELX program suite.

Summary of crystallographic data:

	Urea/2,7-octanedione	**Urea/dimethylformamide**
		
Wavelength	1.4547 Å	1.1698 Å
Crystal dimensions	0.9 x 2.7 x 3.7mm	0.6 x 0.65 x 0.7mm
Unit cell	a=b= 8.1007(5), c= 76.213(5) Å α=β=γ=90°	a= 7.3797(2), b= 9.9588(3), c= 10.9509(2) Å, α= 64.5386(13), β= 77.4999(14), γ= 67.8699(14)°
Temperature/K	30 K	30, 120 K
Refs(total)/Refs(Fo>4σ (Fo))	18206/2529	8093/3359
Data/parameters	2623/363	3632/329
R_{int}	0.1092	0.0364
R_1(Fo>4 σ (Fo))	0.0907	0.0547
***w*R_2**	0.2028	0.1421

The 2,7-octanedione guest has a commensurate relationship with the urea network, facilitated by urea molecules twisted away from the channel walls. The periodicity of the twisted urea molecules is such that a $P6_522$ space group is maintained, with an unusually long *c* axis of 76.3Å as a result. This provided a unique challenge for structure determination by neutron diffraction that was addressed by using an incident wavelength of 1.4547 Å. A complete data set was not collected on OCT but the data were of such quality that anisotropic structure refinement was possible.