

09.2-26 STRUCTURE OF COMPLEXES OF CROWN ETHERS WITH SMALL ORGANIC MOLECULES AND IONS.
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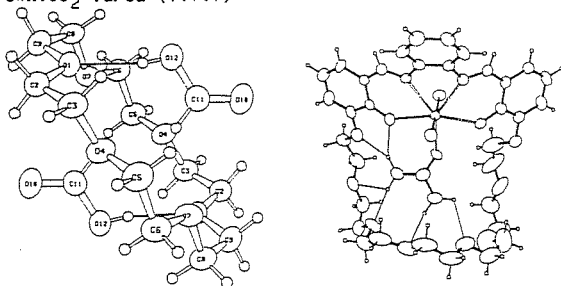
Complexes of crown ethers with inorganic ions are well known. In recent years there is an increasing interest in the bonding of neutral guest species. It has been shown that 18-crown-6 is able to form complexes with organic molecules both in solution and in the solid state (e.g. nitromethane: de Boer et al., J. Am. Chem. Soc., 1982, 104, 4073; urea: Harkema et al., J. Chem. Soc., Chem. Commun., 1981, 368).

In these compounds the bonding between host and guest is effected by means of hydrogen bonds (N-H...O and C-H...O). In the crystal structure of 18-crown-6 formic acid (1:2) (figure) O-H...O and C-H...O interactions are found. The structure is remarkable by the fact that it is the first solid state example of a formic acid molecule with the hydrogens in a *cis* conformation. Complexes of 18-crown-6 with organic molecules are all of the *perching* type, the crown ether ring being too small to accommodate the organic molecule. For this reason 18-crown-6 cannot be used for the selective complexation of organic molecules. Larger ring systems are needed for the complete *encapsulation* of small organic molecules. In our laboratory the structures of a number of complexes of guanidinium salts with larger crown ethers have been determined (Uiterwijk et al., J. Org. Chem., 1986, 51, 1575). In all the complexes a complete encapsulation of the cation by the macrocycle is found. All hydrogens of the guanidinium ion take part in H-bonding to the crown ether.

From the crystallographic work an optimal ring size for complexation can be found with an almost perfect complementary relation between H-bond donors and acceptors. The urea molecule contains both H-bond donors and acceptors. Crown ether molecules usually contain only H-bond acceptors. Therefore, in designing crown ether molecules for the binding of urea, an important factor is the bonding between the urea O-atom and the host molecule. The bonding has been effected in a number of ways.

- protonation of the urea molecule at the O-atom and subsequent complexation with a crown ether (Uiterwijk et al., Angew. Chemie Int. Ed. 19082, 21, 450)
- incorporation of an acid group in the crown ether as an H-bond donor (Aarts et al., J. Am. Chem. Soc. 1986, 108, 5035)
- cocomplexation with Li^+ salts. The Li^+ ion binds the urea oxygen to the crown ether
- combination of crown ether and coordination chemistry. Macrocycles incorporating a Schiff base as part of the ring can be prepared. The Schiff base part forms complexes with metal ions. The coordination of the metal ion can be completed by an O-atom of the urea molecule. This urea molecule is H-bonded to the crown ether part of the molecule.

Crystal structures of urea complexes of the different types have been determined in our laboratory. The figure shows an example of a type d complex: Schiff base crown. UO_2^+ .urea (1:1:1)

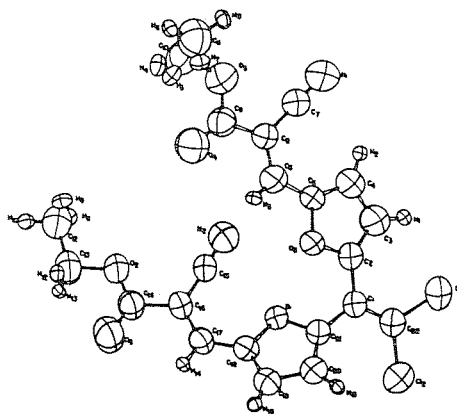


09.2-27 CRYSTAL STRUCTURE OF 1,1(α -CYANO FURAN FURFURYL ACRYLATE)2,2 DICHLOROETHANE.
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The compound ($\text{C}_{22}\text{H}_{16}\text{O}_6\text{N}_2\text{Cl}_2$) crystallized in space group P1. The parameter of the unit cell are: $a=7.87(1)$, $b=12.11(1)$, $c=12.25(1)$ Å, $\alpha=110.26(1)$, $\beta=93.669(1)$ and $\gamma=99.45(1)^\circ$.

A three-dimensional data set was collected at room temperature with $\text{MoK}\alpha$ ($\lambda=0.70926$ Å), using a perpendicular beams diffractometer and the θ - 2θ scan technique, with a graphite monochromator. A total of 2150 reflection different from zero were collected.

The structure was solved by direct methods. The coordinates and the anisotropic temperature factors of the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms were refined by full-matrix least-squares methods to a final R value 0.029.



The molecular structure of $\text{C}_{22}\text{H}_{16}\text{O}_6\text{N}_2\text{Cl}_2$.