Complexes of Crown Ethers with Uronium Salts: Preparation and
Crystal Structure of 18-Crown-6 Uronium Nitrate (1:1) and
Benzo-27-Crown-9 Uronium Perchlorate (1:1)

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As part of our work aimed at the synthesis of molecular receptor molecules for urea we have recently described the first crystalline complex of urea with a macrocyclic polyether *vis.* 18-crown-6 (**1**)^[1,2]. Single-crystal X-ray analysis revealed that in this adduct with a stoichiometry of 5:1 only two urea molecules are coordinated, via two N-H...O hydrogen bonds, to the macrocycle which has in the complex a centrosymmetrical $ag^+a\ ag^-a\ g^+a$ conformation^[3].

We are currently investigating whether the stability of complexes of urea can be enhanced by protonation which is known to occur at the oxygen atom^[5]. Complexes of **1** with uronium nitrate (1:1), uronium picrate (1:1) and uronium *p*-toluenesulfonate (1:2) were pre-

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pared by dissolving 1.5 mmol of **1** and 1.0 mmol of salt in the minimum amount of refluxing methanol. After the addition of twice the volume of chloroform the complexes were precipitated by the addition of diethyl ether. Recrystallization from ethyl acetate/methanol yielded the analytical pure complexes in 50-60 % yield. The 1:1 complex of benzo-27-crown-9 (**2**) with uronium perchlorate was prepared in a different way, *vis.* by equilibration of a solution of 300 mg of **2** in 2 ml chloroform with a solution of 300 mg urea in 2 ml 20% perchloric acid. After separation of the layers, drying over magnesium sulphate and evaporation of the chloroform, the crystalline product was purified by trituration with chloroform. The crystal and molecular structure of two complexes, *vis.* **1**.uronium nitrate (1:1) at 168 K and **2**. uronium perchlorate (1:1) at 269 K were determined by X-ray crystallography using a Philips PW 1100 diffractometer.

Crystal data^[6]. **1**. uronium nitrate (1:1): $C_{13}H_{29}O_{10}N_3$, monoclinic, space group $P2_1/n$, $a = 20.304(9)$, $b = 11.604(6)$, $c = 8.181(3)$ Å, $\beta = 93.95(4)^\circ$, $Z = 4$, $V = 1922.9$ Å³, $D_c = 1.34$ g.cm⁻³, $\mu = 1.00$ cm⁻¹. 3518 reflexions were measured (ω -2 θ scan mode, $\theta < 65^\circ$, graphite monochromated Cu K_α radiation), of which 3185 with $I > \sigma(I)$ (counting statistics) were used for the solution by direct methods (MULTAN^[7]).

2. uronium perchlorate (1:1): $C_{23}H_{41}ClO_{14}N_2$, triclinic, space group $P\bar{1}$, $a = 13.866(5)$, $b = 12.585(7)$, $c = 9.926(6)$ Å, $\alpha = 99.59(3)$, $\beta = 74.91(6)$, $\gamma = 116.52(3)^\circ$, $Z = 2$, $V = 1493.9$ Å³, $D_c = 1.35$ g.cm⁻³, $\mu = 0.20$ cm⁻¹. 5253 reflexions were measured (ω -2 θ scan mode, $\theta < 25^\circ$, graphite monochromated Mo K_α radiation), of which 3145 with $I > \sigma(I)$ (counting statistics) were used for the solution by direct methods (MULTAN^[7]).

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For both structures all hydrogens were located in difference Fourier syntheses. The structures were refined by least-squares methods (ORFLS^[8]; scale factor, isotropic extinction parameter, position parameters, anisotropic thermal parameters for non-H-atoms, isotropic thermal parameters for H) to final weighted R-factors of 6.1% for **1**. uronium nitrate (1:1) and 5.6% for **2**. uronium perchlorate (1:1).

In the first place both structures show that complexation does not affect the site of protonation in urea. A very interesting feature of the structure of **1**.uronium nitrate (1:1) is the rather unusual conformation of the polyether ring ($ag^+a\ ag^-a\ g^+a\ ag^-a\ g^+a$) which differs both from the centrosymmetric conformation of the macrocyclic ring in the **1**.urea (1:5) complex ($ag^+a\ ag^-a\ g^+a$)^[9] and from the centrosymmetric conformation of the crown in the **1**.*S*-*tert*-butylthiuronium perchlorate (1:2) complex ($ag^+a\ ag^-a\ ag^+a$)^[11]. The conformation of the ring in the **1**.uronium nitrate (1:1) complex has been found before in the 1:1 complexes of **1** with $Nd(NO_3)_3$ ^[12] and with $La(NO_3)_3$ ^[13], but has not been observed previously in complexes of **1** with organic salts^[14].

In the **1**.uronium nitrate (1:1) complex there are three N-H...O hydrogen bonds, namely between the uronium cation and the O(1), O(2) and O(4) oxygen atoms of the macrocyclic ring. This type of bonding can be regarded as a combination of the hydrogen bonding present in the **1**.urea (1:5) complex with bonding via two adjacent oxygen atoms^[1] and in the **1**.*S*-*tert*-butylthiuronium perchlorate (1:2) complex with bonding via two alternating oxygen atoms^[11]. The three hydrogen bonds between the host and guest force the crown ether in such a conformation that both faces of the macrocyclic

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have very different coordinating properties (figure 1). This prevents complexation of a second molecule at the opposite face of the macrocyclic^[14].

Figure 1. Top and side view (ORTEP^[15]) of the 18-crown-6.uronium nitrate (1:1) complex. Hydrogen bonds are indicated.

In the **2**.uronium perchlorate (1:1) complex the binding between host and guest is completely different from the situation described above. The cation is totally encapsulated within the macrocycle with its molecular framework almost coincident with the best plane defined by the crown oxygens. The polyether ring has the conformation $asa\ ag^-g^-ag^+a\ ag^-a\ ag^-g^-ag^+a\ ag^-a\ ag^-g^-g^-g^-a$, where "s" (synperiplanar) denotes the torsion angle of almost 0° , imposed by the benzo-substituent.

All five uronium hydrogen atoms are used for hydrogen bonding to crown oxygens (figure 2). It is interesting to note that the oxygen atoms adjacent to the benzo-substituent are not used in hydrogen bonding, possibly as a result of the electron-withdrawing effect of the benzo group. Although the conformation of the macrocyclic

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rather different from the conformation in the isoelectronic 2. guanidinium perchlorate (1:1) complex^[16] (asa $ag^+a\ g^-g^-ag^-a\ ag^-g^-ag^+a\ g^+g^+a\ ag^-a\ ag^-a$), the positions of the crown oxygens not adjacent to the benzo-ring are quite the same relative to the central cation. The most pronounced difference is the "bowl"-shaped structure of the crown in the guanidinium complex, compared with a much flatter uronium complex (figure 2), presumably a result of the sixth hydrogen bond in the guanidinium complex.

Figure 2. Top and side view (ORTEP^[15]) of the benzo-27-crown-9-uronium perchlorate (1:1) complex. Hydrogen bonds are indicated.

The results presented in this paper demonstrate that in the complexes of crown ethers with polyfunctional organic cations the macrocyclic ring can adopt a number of different conformations, varying with the type of cation and with the nature of the anion of the salt^[14,16]. The two structures determined show two different kinds of bonding between host and guest. In the smaller ring (18-crown-6) the intramolecular cavity is too small to accommodate the uronium ion. In this case three N-H...O hydrogen bonds are formed

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between the uronium ion and the macrocycle. Furthermore a N-H...O and a short O-H...O (2.48 Å) hydrogen bond are present between cation and anion, indicating an appreciable interaction between these ions. In the larger ring (benzo-27-crown-9) the cation is completely encapsulated by the macrocycle. All hydrogen bonds present are between cation and macrocycle including a short O-H...O hydrogen bond of 2.53 Å^[17]. The results of these structure determinations are in accordance with a much higher lipophilicity of the "encapsulated" complex compared with the "nesting" conformation of the 1. uronium nitrate (1:1) complex. Consequently the benzo-27-crown-9 (2) is capable of transferring the uronium salt virtually completely to the chloroform layer. In the absence of 2 no uronium perchlorate is transferred from the aqueous to the organic phase. This information will be utilized in the synthesis of specific molecular receptor molecules with built-in acid groups for urea.

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