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Preparation and Structure of the 18-Crown-6 • 2(Chloral Hydrate) Complex

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18-Crown-6 forms a stable 1:2 host-guest complex with chloral hydrate. This complex is not dissociated in non-polar solvents.

Although Pedersen reported the formation of complexes between 18-crown-6 and neutral molecules in 1971,[1] this type of complexation has only recently attracted attention.[2] On the other hand, the capacity of chloral and chloral hydrate to form molecular complexes is well known.[3] We report here the formation of a well defined complex between 18-crown-6 and chloral hydrate.

The complex was prepared in a straightforward manner: 18-crown-6 (1, 4 mmol, 1.06 g) and chloral hydrate (2, 8 mmol, 1.32 g) were dissolved in THF (20 ml) and the solution was stirred for 15 min. The clear solution was kept at 0-5 °C until no further crystallization was noticed. The crystals were filtered and dried under vacuum. The average yield was 1.91 g (80%). The melting point of the complex 3 (112-114 °C) is well above the melting point of 2 (57 °C) or the one of 1 (43-45 °C). The complex is stable at room temperature. The elemental analysis established the 1:2 (1 : 2) stoichiometry of the complex. Found: C, 32.10; H, 5.16; Cl, 35.05%. Calcd for $C_{16}H_{30}Cl_6O_{10}$: C, 32.39; H, 5.08; Cl, 35.75%.

Many comprehensive physical researches confirmed the gem-diol structure of 2.[3] However in spite of the stability of chloral hydrate, its solutions are not stable. It is apparent from the IR spectra that in organic solvents there is present an equilibrium between chloral hydrate 2, chloral 4 and water. The solution spectra of 2 contain several bands due to O-H vibrations (3100-3700 cm^{-1}); the spectra also show a strong absorption band at 1770 cm^{-1} (ν_{CO} of 4) and a weak band near 1605 cm^{-1} (δ_{OH} in-plane of H_2O). Crystal structure determination[4] and infrared spectra[3] in the solid state proved the gem-diol structure

$$\underset{\underline{2}}{CCl_3-CH(OH)_2} \rightleftharpoons \underset{\underline{4}}{CCl_3-CH=O} + H_2O$$

of solid 2. The high-frequency region of vibrational spectra of the complex 3 contain bands due to hydrogen bonded ν_{OH} (3360 cm^{-1} in Nujol, 3370 cm^{-1} in KBr and 3290 cm^{-1} in chloroform). The O-H vibration is also seen in the Raman spectrum at 3380 cm^{-1}. The band at 1760 cm^{-1} and 1605 cm^{-1} which indicate the decomposition of the gem-diol into chloral and water are absent in spectra of the complex in solid state (KBr disk, Nujol and Raman) and in solution in $CHCl_3$.

These data indicate that the complex does not dissociate in the solid state or in solution in non-polar organic solvents. Both the frequencies and spectral activity of the crown ether bands in the IR and Raman spectra of the complex are comparable to those found in many complexes in which the crown is known to have the D_{3d} symmetry.[5] The CH_2 rocking vibration at 960 cm^{-1} and the C-C stretching at 835 cm^{-1} are characteristic of this regular symmetry.

It is also apparent from the ^1H NMR spectrum of 2 that in $CDCl_3$, there is an equilibrium between 2, 4 and water. This spectrum shows three signals, at 4.2 ppm (OH of 2 and water), at 5.32 ppm (CH of 2) and at 9.06 ppm (CH=O of 4). The ^1H NMR spectrum of the complex in the same solvent shows three signals. The signal of the crown which appear at 3.67 ppm (singlet) in the free crown is slighly shifted downfield (3.72 ppm) in the complex. The triplet (J=5 Hz) at 5.65 ppm is assigned to the CH in chloral hydrate; it is noteworthy that this signal is markedly shifted to lower field (0.33 ppm) upon complexation. The concentration dependent doublet (J=5 Hz) at 5.5 ppm is attributed to the OH of the gem-diol. The integration further confirm the 1:2 stoichiometry of the complex. In ^{13}C NMR, the chemical shift of the crown carbon (70.02 ppm) is close to the shift of the free crown carbons in the same solvent ($CDCl_3$). There are two peaks at 94.21 and 102.12 ppm. The high-field peak, which is a doublet in the coupled spectrum ($^1J_{CH}$=173.9 Hz) is assigned to the CH and the weak low-field peak is assigned to the CCl_3 of the gem-diol. Thus the NMR spectra also confirm that the complex is not dissociated in non-polar organic solvents.

Chloral hydrate has both essential feature to form a complex with a crown ether. It has a dipole moment (2.65 D in dioxan)[6] and its hydrogen bonding capacity is very good. Figure 1 shows the proposed structural model for the complex.[7] Host and guest molecules are held together through hydrogen bonds and dipole-dipole interactions.

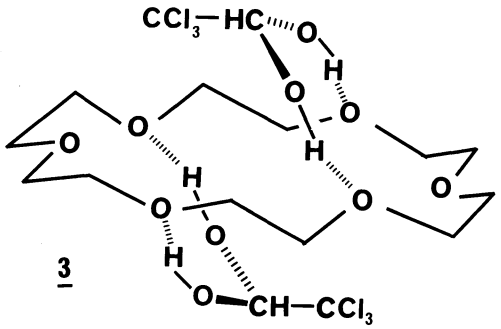

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Fig. 1. Structural model for the 18-crown-6 • 2 (chloral hydrate) complex.

References

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7) It has been so far impossible to grow a crystal of the complex suitable for X-ray structure determination.

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