

**A Ternary Molecular Inclusive Complex from  
Crown Ether, Cyclodextrin and Potassium  
4-nitrophenolate Formation and  
Spectroscopic Studies**

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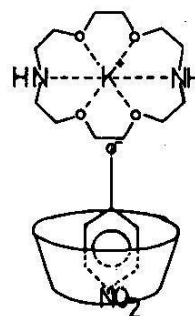
Cyclodextrins (cycloamyloses), a series of oligosaccharides, are macrocyclic molecules containing glucopyranose units connected by  $\alpha$ -1, 4-linkages. Both the rims of their taurus shape consist of polar hydroxy groups while the centre of the molecule is relatively non-polar. The central cavity of cyclodextrin can include a variety of molecules and extensive studies about inclusion compounds with cyclodextrins have been reported [1]. Crown ethers are the macrocycles containing a central cavity internally lined with polar binding sites and externally with non-polar-CH-groups. Such crown compounds form stable complexes with cations of alkali and alkaline earth metals [2].

By making use of hydrophobic and hydrophilic cavities of a cyclodextrin and a crown ether respectively, we herein report for the first time [3] synthesis and spectroscopic studies [4] of a ternary inclusive complex

made from a crown ether\*, potassium 4-nitrophenolate, and  $\beta$ -cyclodextrin.

Equimolar amounts of diaza-18-crown-6 and potassium-4-nitrophenolate were

dissolved in methanol. The solution was warmed to accomplish complete dissolution of the reactants. Yellow crystals were isolated upon cooling the solution. The ternary complex was prepared by dissolving 113 mg (0.1 mM) of  $\beta$ -cyclodextrin and 43.9 mg (0.1 mM) of [K(diaza 18-C-6)] 4-nitrophenolate in 3 ml of deionized water. The reaction mixture was heated to 60°C and then was gradually cooled to 10°C. Addition of a few drops of acetone in the cold solution gave yellow microcrystals of the desired product.



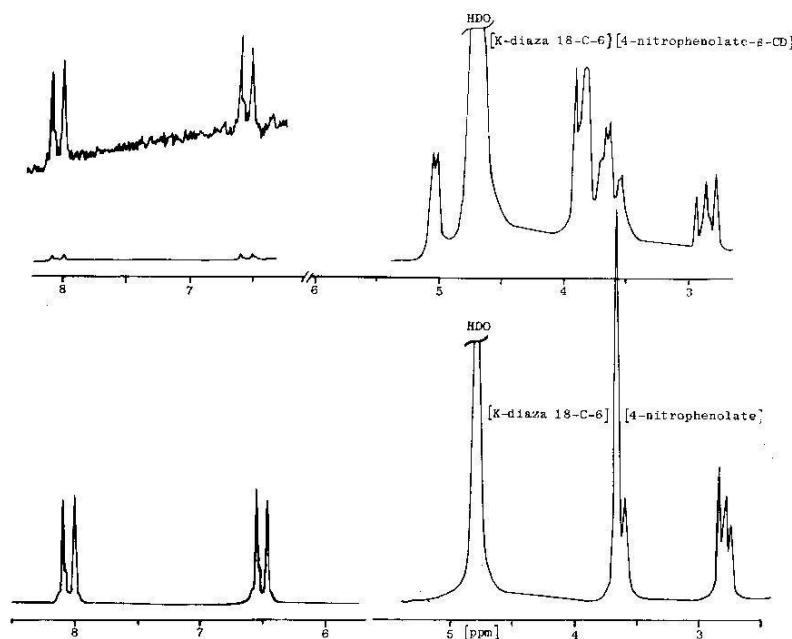
The infrared C-O-C stretching frequency absorption band was recorded at 1120  $\text{cm}^{-1}$  in free host crown ether where as upon complexation it was shifted to lower energy (1106  $\text{cm}^{-1}$ )

\* Diaza-crown ether was synthesized in our laboratory; O.A.Gansow, A.R.Kausar and K.B.Triplett, *J. Heterocyclic Chem.*, **18**, 297 (1981).  $\beta$ -Cyclodextrin was purchased from Sigma Chemical Co. USA. Elemental analysis of complexes were performed on a Carlo Erba model 110 Elemental Analyser at HEJ Research Institute of Chemistry, University of Karachi, Pakistan. These were all satisfactory. Infrared spectra were recorded using either a Unicam SP-200 G or a Jasco IRA-1 infrared spectrophotometer. NMR spectra in  $\text{D}_2\text{O}$  were recorded on a Bruker WP-100 SY at 100 MHz using DSS as an internal standard.

indicating [5] the potassium cation interacting with heteroatoms of crown ether. It has already been established [6] that 4-nitrophenolate binds preferentially with nitro end into the cavity of cyclodextrins. Asymmetric and symmetric strong absorption bands due to nitro group were recorded at 1590 and 1325  $\text{cm}^{-1}$  respectively in potassium 4-nitrophenolate whereas in potassium-crown ether complex these were found at 1578 and 1296  $\text{cm}^{-1}$ . Upon ternary complex formation, nitro absorption bands were displayed at 1578 and 1287  $\text{cm}^{-1}$  as sharp and weak bands but well distinguished from any of the host cyclodextrin infrared bands.

The  $^1\text{H}$ -nmr spectrum of diaza 18-C-6 in  $\text{D}_2\text{O}$  displays three sets of signals at  $\delta$  2.78 (t),  $\delta$  3.68 (t), and  $\delta$  3.70 (s) ppm due to  $\text{N-CH}_2$ ,  $\text{O-CH}_2$ , and  $\text{O-CH}_2 - \text{CH}_2 - \text{O}$  protons respectively. In its complex with potassium [7]

$\text{N-CH}_2$  protons signal was recorded at  $\delta$  2.80 ppm, all  $\text{O-CH}_2$  protons at  $\delta$  3.65 ppm. The aromatic protons of 4-nitrophenolate moiety in potassium-crown ether complex were recorded at  $\delta$  6.51 (d, ortho) ppm, and at  $\delta$  8.05 (d, meta) ppm. The pmr spectrum of the ternary complex displayed in the figure shows that proton signals which are indicative of diaza 28-C-6,  $\beta$ -cyclodextrin and 4-nitrophenolate moieties. Aromatic protons of 4-nitrophenolate which is now included in  $\beta$ -cyclodextrin cavity were recorded at  $\delta$  6.55 and  $\delta$  8.05 ppm, and the findings are in agreement with the results of Bergeron and co-workers who reported that in 4-nitrophenolate  $\beta$ -cyclodextrin system, no large shifts were observed upon complexation [8]. Crown ether protons were recorded at  $\delta$  2.85 ( $\text{N-CH}_2$ ) and  $\delta$  3.65 ( $\text{O-CH}_2$ ) ppm whereas cyclodextrin protons were observed between the region of  $\delta$  3.5 and  $\delta$  5.1 ppm.



$^1\text{H}$ -nmr spectra in  $\text{D}_2\text{O}$  of  $[\text{K}(\text{diaza } 18\text{-C-6})]\text{-4-nitrophenolate}$  and its complex (ternary) with  $\beta$ -cyclodextrin.

An X-ray crystallographic study of the potassium ternary complex is underway and further work is being carried out to isolate similar type of inclusive complexes.

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#### References

1. (a) M.L.Bender and M.Komiyama, *Cyclodextrin Chemistry*, Springer, Berlin, 1978.
- (b) W.Saenger, *Angew.Chem.Intl.Ed.*, **19**, 344 (1980).
2. J.J.Christensen, P.J. Eatough and R.M.Izatt, *Chem.Rev.*, **74**, 351 (1974)
3. F.Vogtlem, H.Pff, E.Friedrichs and W.M.Muller, *Angew.Chem.Int.Ed.*, **21**, 431 (1982)
4. M.Sc. thesis of S.Mohammad, Punjab University in (1982)
5. R.B.King and P.R.Heckley, *J.Amer.Chem.Soc.*, **96**, 3118 (1974)
6. (a) R.J.Bergeron, M.A. Channing, G.J. Gibeily and D.M.Pillor, *J.Amer.Chem.Soc.*, **99**, 5146 (1977).  
(b) M.R.Eftink and J.C.Harrison, *Bioorg.Chem.*, **10**, 388 (1981)
7. A.Knochel, J.Oehler, G.Rudolph and V.Sinnwell, *Tetrahedron*, **33**, 119 (1977)
8. R.Bergeron and R.Rowan, *Bioorg.Chem.*, **5**, 425 (1976).