

## Uranyl Complexes of Some Crown Ethers

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Reactions of hydrated uranyl salts with 18-crown-6 to form uranyl complexes have been reported [1, 2], in which only complexes with a 1:1 uranyl to crown ratio were obtained. Our investigation of the reaction of uranyl chloride with a number of crown ligands has produced complexes whose stoichiometry varies depending on the crown used and the absence or presence of water in the system. When hydrated uranyl chloride is used only 1:1 complexes are formed. Under anhydrous conditions the metal to crown ratio varies from 2:3 to 2:1 depending upon the crown employed.

## Experimental

### General

Dibenzo-18-crown-6 and dicyclohexyl-18-crown-6 were purchased from Strem Chemicals, while 18-crown-6 and 15-crown-5 were obtained from PCR, Inc. The preparation of 12-crown-4 was from a literature procedure [3]. Reagent quality anhydrous and hydrated uranyl chloride was obtained from Alfa Products. Anhydrous complexes were prepared and handled in a Vacuum Atmospheres Corporation controlled atmosphere glove box. Infrared spectra were recorded on a Perkin Elmer 621 spectrometer. Analyses were performed by the Analysis Branch of the Phillips Research and Development Department.

### Preparation of Hydrated Complexes

Glacial acetic acid solutions (10 ml) of uranyl chloride trihydrate and polyether in equimolar amounts (varying from 0.0027 to 0.0045 mol) were combined and stirred for approximately 30 minutes. The resulting mixture was filtered, and the collected precipitate was washed with diethyl ether and dried under vacuum.

### Preparation of Anhydrous Complexes

These reactions were made similarly to the above procedure except anhydrous uranyl chloride and a solvent system of glacial acetic acid containing 5% acetic anhydride was used.

## Results and Discussion

When acetic acid solutions of 18-crown-6, 15-crown-5 or 12-crown-4 and uranyl chloride trihydrate are mixed, a yellow precipitate forms immediately. The analytical results and the assigned stoichiometry of the complexes are given in Table I. All three complexes have a 1:1 uranyl to crown ratio. Selected bands from the infrared spectra are listed in Table II. Water in the complexes is indicated clearly by the presence of the O–H stretching and bending vibrations near 3200 and 1610  $\text{cm}^{-1}$  respectively. In the 18-crown-6 and 15-crown-5 complexes the C–O–C stretching vibrations are lowered 20–25  $\text{cm}^{-1}$  compared to the uncomplexed crown. Such a shift is indicative of coordination to a polyether by a metal ion [4]. In the 12-crown-4 complex the C–O–C stretching vibration region is complex and the C–O–C stretch cannot be assigned with any degree of certainty. The assignments for the U–O stretching and bending modes of the uranyl group and the stretching vibration for the U–Cl bond are consistent with previous work on uranyl complexes [5, 6].

At this stage of our work we were surprised that the uranyl to crown ratio had remained constant. It was anticipated that the variation in polyether cavity size would change the uranyl ion to crown ratio. Since these complexes dissociate in the presence of excess water, we felt that a stoichiometric amount of water might be influencing the complex formation.

The above reactions were repeated using an anhydrous system and the analytical results with the proposed formulations for the complexes isolated are tabulated in Table I. The results show that the exclusion of water from these complexes causes the uranyl to polyether ratio to vary as the polyether ring size changes. Both the unsubstituted 18-crown-6 and its dicyclohexyl analogue have a 2:1 ratio. However, under the same conditions dibenzo-18-crown-6 does not form an uranyl chloride complex. Similar results have been reported [7] previously. While the benzene substituents might decrease the basicity of the polyether enough to prevent complex formation, one cannot discount steric factors. Recent X-ray structure determinations [8, 9] have shown that the uranyl ion does not lie in the cavity of its 18-crown-6 complex. Thus the benzene rings could restrict internal mobility of the polyether, so that the desired conformation for complex formation is not as accessible. The uranyl to crown ratio decreases when the smaller 15-crown-5 is used, but the 12-crown-4 complex retains the 1:1 ratio of its hydrated analogue.

The infrared data for the anhydrous complexes are summarized in Table II. Again a shift of the

TABLE I. Analytical Data for Uranyl Crown Complexes.

Complex	Calcd %			Found %		
	C	H	Cl	C	H	Cl
UO <sub>2</sub> Cl <sub>2</sub> ·(18-crown-6)·3H <sub>2</sub> O	21.86	4.60	10.75	21.82	4.68	10.80
UO <sub>2</sub> Cl <sub>2</sub> ·(15-crown-5)·3H <sub>2</sub> O	19.52	4.27	11.52	19.50	4.38	11.51
UO <sub>2</sub> Cl <sub>2</sub> ·(12-crown-4)·2H <sub>2</sub> O	17.37	3.65	12.82	17.58	3.20	12.86
(UO <sub>2</sub> Cl <sub>2</sub> ) <sub>2</sub> ·(18-crown-6)	15.23	2.56	14.99	15.57	2.69	14.96
(UO <sub>2</sub> Cl <sub>2</sub> ) <sub>2</sub> ·(dicyclohexyl-18-crown-6)	22.78	3.45	13.45	23.30	3.42	13.39
(UO <sub>2</sub> Cl <sub>2</sub> ) <sub>2</sub> ·(15-crown-5) <sub>3</sub> ·2HCl	25.45	4.42	15.02	25.42	4.47	15.34
UO <sub>2</sub> Cl <sub>2</sub> ·(12-crown-4)	18.58	3.12	13.71	18.90	3.38	15.95

TABLE II. Infrared Data for Uranyl Crown Complexes in cm<sup>-1</sup>.

Complex	$\nu(\text{C-O-C})^a$	$\nu(\text{O-U-O})$	$\delta(\text{O-U-O})$	$\nu(\text{U-Cl})$
UO <sub>2</sub> Cl <sub>2</sub> ·(18-crown-6)·3H <sub>2</sub> O	1085 (1111)	915	255	242
UO <sub>2</sub> Cl <sub>2</sub> ·(15-crown-5)·3H <sub>2</sub> O	1090 (1110)	925	260	237
UO <sub>2</sub> Cl <sub>2</sub> ·(12-crown-4)·2H <sub>2</sub> O	—	938	268	233
(UO <sub>2</sub> Cl <sub>2</sub> ) <sub>2</sub> ·(18-crown-6)	1085 (1111)	913	262	234
(UO <sub>2</sub> Cl <sub>2</sub> ) <sub>2</sub> ·(dicyclohexyl-18-crown-6)	1065 (1110)	915	263	235
(UO <sub>2</sub> Cl <sub>2</sub> ) <sub>2</sub> ·(15-crown-5) <sub>3</sub> ·2HCl	1083 (1110)	918	258	233
UO <sub>2</sub> Cl <sub>2</sub> ·(12-crown-4)	1092, 1070 (1133, 1095)	936	265	238

<sup>a</sup>  $\nu(\text{C-O-C})$  for uncomplexed crown is in parentheses.

C-O-C stretching vibrations in the complexes to lower wave number relative to its position in the "free" crown is observed. The assignments of the uranyl ion vibrations and the U-Cl stretch are analogous to those in the hydrated complexes. The uranium to polyether oxygen stretching frequency is expected in the 300–500 cm<sup>-1</sup> range, but no assignment has been made as the bands in this region are weak and contain ligand vibrations.

The complexes are not stable in polar solvents. Any of these solvents that dissolved the complexes also caused them to dissociate. <sup>1</sup>H and <sup>13</sup>C NMR studies of these complexes in methanol or water showed no shift in the methylene protons or carbons, respectively, of the "free" crown ethers compared to the uranyl crown solutions. A similar <sup>1</sup>H NMR study of nickel, cobalt and copper 18-crown-6 complexes [4] showed upfield shifts of the methylene protons of the coordinated crown.

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