

## COMPLEXES OF SOME MACROCYCLIC POLYETHERS WITH ALKALI METALS

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Crystalline complexes of benzo-18-crown-6, 4-nitrobenzo-18-crown-6, dibenzo-30-crown-10 and dimethyl dibenzo-30-crown-10 with potassium, rubidium, and cesium thiocyanates were prepared. The stability constants of the complexes of these crown-compounds with the potassium and sodium ions in methanol were measured.

In our earlier paper<sup>1</sup> we demonstrated the possibility of applying some macrocyclic polyethers, called crown-compounds, as neutral carriers in ion-selective electrodes for potassium. An investigation of the relationship between the structure of the crown-compounds and the selectivity of the corresponding electrode membranes has revealed<sup>2</sup> that the highest selectivity for potassium with respect to sodium among the crown-compounds with eighteen-membered ring was exhibited by benzo-18-crown-6 and 4-nitrobenzo-18-crown-6. Among the crown-compounds with larger rings the optimum properties were found for dibenzo-30-crown-10, and for dimethyl-dibenzo-30-crown-10 in the first place<sup>3</sup>. For a deeper insight into the structural effects on selectivity a knowledge of the structure of isolated complexes and their stability in solution is desirable. We report here the preparation of the crystalline complexes of selected crown-compounds with cations suited for uses in the X-ray structure analysis and the determination of the stability constants of potassium and sodium complexes.

### EXPERIMENTAL

*Chemicals.* Benzo-18-crown-6, dibenzo-30-crown-10 and dimethyl dibenzo-30-crown-10 were prepared according to ref.<sup>3,4</sup>. Rubidium and cesium thiocyanates were obtained by neutralization of hydroxides with a solution of thiocyanic acid followed by evaporation. The respective hydroxides and thiocyanic acid were obtained from the available salts by means of ion exchangers. The other chemicals were reagent grade. Methanol used for measuring the stability constants contained 0.07% of water.

*4-Nitrobenzo-18-crown-6.* A solution of 1.12 g (0.02 mol) potassium hydroxide in 20 ml butanol was added to 1.55 g (0.01 mol) of 4-nitropyrocatechol in 10 ml of butanol in an inert atmosphere. To a suspension of partly precipitated potassium salt of 4-nitropyrocatechol 2.75 g (0.01 mol)

TABLE I  
Properties of the Complexes of Crown-Compounds with Alkali Metal Thiocyanates

Crown-compound (m.p., °C)	MSCN	M.p., °C	Formula (mol.w.)	% N found/calc.
Benzo-18-crown-6 (41—42)	KSCN	132—133	C <sub>17</sub> H <sub>24</sub> O <sub>6</sub> NSK (409·5)	3·42 3·41
	RbSCN	144—145	C <sub>17</sub> H <sub>24</sub> O <sub>6</sub> NSRb (455·8)	3·07 3·07
	CsSCN	146—147	C <sub>17</sub> H <sub>24</sub> O <sub>6</sub> NSCs (503·3)	2·67 2·78
4-Nitrobenzo-18-crown-6 (83—84·5)	KSCN	159—160	C <sub>17</sub> H <sub>23</sub> O <sub>8</sub> N <sub>2</sub> SK (454·5)	6·10 6·16
	RbSCN	178—179	C <sub>17</sub> H <sub>23</sub> O <sub>8</sub> N <sub>2</sub> SRb (500·8)	5·49 5·59
	CsSCN	174—175	C <sub>17</sub> H <sub>23</sub> O <sub>8</sub> N <sub>2</sub> SCs (548·3)	5·16 5·10
Dibenzo-30-crown-10 (104—105)	KSCN	138—139	C <sub>29</sub> H <sub>40</sub> O <sub>10</sub> NSK (633·8)	2·26 2·20
	RbSCN	120—121	C <sub>29</sub> H <sub>40</sub> O <sub>10</sub> NSRb (680·1)	1·91 2·05
	CsSCN	111—112	C <sub>29</sub> H <sub>40</sub> O <sub>10</sub> NSCs (727·6)	1·93 1·92
Dimethyldibenzo-30-crown-10 (77—78)	KSCN	127—130	C <sub>31</sub> H <sub>44</sub> O <sub>10</sub> NSK (661·8)	2·02 2·11
	RbSCN	103—104	C <sub>31</sub> H <sub>44</sub> O <sub>10</sub> NSRb (708·1)	2·13 1·97
	CsSCN	111—112	C <sub>31</sub> H <sub>44</sub> O <sub>10</sub> NSCs (755·6)	1·83 1·85

TABLE II  
Stability Constants of the Complexes of Crown-Compounds with Potassium and Sodium Ions

Crown-compound	log K <sub>KC</sub>	log K <sub>NaC</sub>
Benzo-18-crown-6	5·05 ± 0·12	4·53 ± 0·04
4-Nitrobenzo-18-crown-6	4·71 ± 0·12	3·95 ± 0·09
Dibenzo-30-crown-10	4·23 ± 0·08	2·80 ± 0·04
Dimethyldibenzo-30-crown-10	4·67 ± 0·07	2·52 ± 0·20

of 1,14-dichloro-3,6,9,12-tetraoxatetradecane was added. The reaction mixture was heated 16 h to a mild reflux with stirring and purging with nitrogen. The potassium salt of 4-nitroprocatechol gradually dissolved during the reaction, and the originally red colour of the reaction mixture changed into yellow. On completion of the reaction potassium chloride was filtered off, and butanol was removed by distillation *in vacuo*. The yellow-brown oily residue was chromatographed on a column of aluminium oxide (Woelm) by elution with a benzene-ether mixture (1 : 1) with 1% methanol added. The process of the isolation of the crown-compound was followed by TLC on aluminium oxide; detection with Dragendorff's reagent,  $R_F$  0.6. By evaporation of chromatographic fractions containing the product and recrystallization from the benzene-hexane mixture, 0.5 g (14% theor.) of 4-nitrobenzo-18-crown-6 in the form of slightly yellowish leaflets was obtained, m.p. 83–84°C. For  $C_{16}H_{23}O_8N$  (357.3), calculated: 53.77% C, 6.48% H, 3.91% N; found: 53.82% C, 6.45% H, 3.78% N;  $M^+$  357.

**Preparation of complexes.** 0.2 mmol of thiocyanate was dissolved in the lowest possible amount of hot methanol (c. 0.1 ml). 0.2 mmol of crown-compound dissolved in 2 ml of hot ethyl acetate was added to the solution. The solution was left overnight, and the separated crystals of the complex were filtered off. In those cases when the complex did not crystallize the solution was concentrated *in vacuo* to about one third of the volume, and left again to crystallize on addition of 2 ml of ethyl acetate. In some cases the isolated complexes were recrystallized from ethyl acetate. The yields of the less soluble complexes of 18-crown-6 compounds were 80–85%, of more soluble 30-crown-10 compounds 50–70% theor. The properties of crystalline complexes are given in Table I.

**Measurement of the stability constants of complexes.** The stability constants were determined potentiometrically by using glass cation-sensitive electrodes. The potassium electrode was prepared from the NAS 27–5 glass, the sodium electrode was made of the NAS 20–10 glass (University of Leningrad, Department of Physical Chemistry). Silver-silver chloride wire electrode in 0.1M-KCl or NaCl was used as the internal electrode. The measurement was carried out at 25°C against saturated calomel electrode with a salt bridge 0.01M- $NH_4NO_3$  with an asbestos fibre junction. The corresponding calibration curves were constructed for both electrodes with methanol solutions of alkali metal chlorides. For the determination of the constants, the EMF of the methanol solution of a known amount of potassium or sodium chloride was measured each time after addition of a solid crown-compound. The concentration of the ligand was gradually increased by five increments up to the final two- to fourfold molar excess. The stability constants were evaluated from the total metal ion concentration, concentration of the ligand added, and the measured equilibrium concentration of the free metal ion.

## RESULTS AND DISCUSSION

Preparation of complexes of selected crowns with alkali metal salts by a procedure described by Pedersen<sup>4</sup> in methanol medium was not successful. The complexes from a methanol solution of both components did not crystallize directly, and the melting points of the crystalline residue after evaporation of methanol were the same as those of the original crown-compounds. On the other hand, good results were obtained with ethyl acetate as solvent. Because of their solubility in ethyl acetate, alkali metal thiocyanates were chosen as the complex-forming component. In this way good crystalline complexes were obtained, which according to the analytical results have a stoichiometric composition polyether-metal salt 1 : 1. The melting

points of the complexes are always higher than those of the parent crown-compounds. The complexes of rubidium and cesium with eighteen-membered crown-compounds melt at higher temperatures than those with potassium, while the results obtained for a crown-compound with the thirty-membered ring were just opposite.

The stability constants for the complexes of crown-compounds with potassium ( $K_{KC}$ ) and sodium ( $K_{NaC}$ ) are given in Table II. It can be seen from the experimental data that the stability of the complexes of eighteen-membered crown-compounds is higher than that of the thirty-membered ones, which is more evident in the case of complexes with sodium. The different stability of the complexes is probably related to the difference in their structure. The structural factors are also the cause of the finding that the stability constants ratio of potassium and sodium complexes of eighteen-membered crown-compounds does not reflect their selectivity in the case of application for ion-selective electrodes which is approximately fifty times higher. These problems are the object of a further study.

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