recently observed that in methanesulfonic acid–water mixtures the solvent composition at which the coil-to-helix transition of poly-L-glutamic acid occurs does not change upon changing the molecular weight of the polymer over a wide range.[6]

There is an additional factor which may account for the differences between the two polymers. Noncovalent bonds among side chains might contribute differently to the conformational stability of PCHA and PLP. Already it has been shown that noncovalent interactions like hydrophobic bands among side chains are responsible for the enhanced conformational stability of PLP in aqueous solutions.[4] It is presently well known that nonpolar paraffin chains in aqueous solutions form hydrophobic bonds and tend to aggregate, the driving force for aggregation being the increase of entropy or decrease of order of the water structure involved in the process.[21,22]

Strong acids like sulfuric acid do resemble water very closely in the fact that they possess a structure in which acid molecules are very strongly hydrogen bonded.[23,24]

Long-chain fatty acids form micelles in concentrated sulfuric acid and in sulfuric acid–water mixtures. It was shown that this phenomenon is due to the favorable entropy changes going from individual fatty acid molecules with solvent highly organized around the paraffin chain to micelles where the aggregation decreases the order of the solvent structure.[25]

Micelle formation studies in methanesulfonic acid are not reported in the literature, but very probably noncovalent bonds between nonpolar solutes might form in this acid and in acid–water mixtures as well.

Therefore it is possible that the attitude of the cyclohexane side chains of PCHA to form "acidophobic" bonds is different from that of the phenyl groups of PLP. In this respect one might observe that the side chains of PCHA are much less polar than the side chains of PLP. Phenyl groups can in fact be considered nonpolar only when they are viewed parallel to the plane of the ring; both faces of the ring are polar. As a consequence there is the possibility that stronger noncovalent bonds are formed in PCHA than in PLP. This fact could enhance the stability of the α-helical structure of PCHA, with respect to PLP, in spite of the unfavorable steric interference between the side chains and the peptide backbone.

Acknowledgments. The authors express their gratitude to Professor Ernesto Scoffone for continuous and stimulating discussions during this work, and to Professor Joseph Steigman, Polytechnic Institute of Brooklyn, for useful suggestions at the beginning of this research.

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Crystalline Salt Complexes of Macrocyclic Polyethers

C. J. Pedersen

Contribution No. 209 from the Elastomer Chemicals Department,
Experimental Station, E. I. du Pont de Nemours and Company, Inc.,
Wilmington, Delaware 19898. *Received February 19, 1969*

Abstract: The stoichiometry of the crystalline complexes of sodium, potassium, ammonium, rubidium, cesium, and barium salts with the subject polyethers has been investigated in greater detail. Depending on the relative sizes of the "hole" in the cyclic polyether and of the cation, complexes with polyether:cation mol ratios of 1:1, 3:2, or 2:1 are obtained. The 2:1 and 3:2 complexes might possibly be "sandwich" structures. By preferential complex formation in methanol, potassium and cesium ions have been separated almost quantitatively.

The preparation and properties of a number of macrocyclic polyethers have been described previously.[1] Due to the cumbersomeness of the nomenclature of these compounds, a simplified method of naming them,[1] as shown by the examples in Figure 1, will be used.

Certain polyethers, particularly those containing 5 to 10 oxygen atoms each separated from the next by 2 carbon atoms, were shown to form crystalline complexes of alkali and alkaline earth salts, such as chlorides, iodides, and thiocyanates. It was originally reported that the stoichiometry of these complexes is always one molecule of polyether per ion regardless of its valence. It is the purpose of this paper to report that more recent work indicates that the stoichiometry is not as simple as previously assumed.

Some indication that the stoichiometry is not strictly 1:1 is evident in the published data.[1] For example, in Table VII[1] the ratio of moles of XXVIII dissolved per mole of cesium thiocyanate is given as 1.20, indicating that a mole of this salt interacts with more than a mole of the polyether in methanol. In Table XIV,[1] whereas the melting points of the XXVIII complexes of sodium, potassium, ammonium, and rubidium thiocyanates are sharp, that of the cesium salt is unsatisfactory. Also, Pressman found that a rubidium ion can interact in solution with more than a single molecule of dicyclohexyl-18-crown-6.[2]

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(1) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

A systematic overestimation of the diameters of the "holes" in the cyclic polyethers, based on van der Waals radii, decisively influenced the earlier conclusions. The original estimates and the more correct values for the diameters are shown in Table I.

Table I. Diameters of Holes, Å

Polyethers	Original estimates	Revised
All 14-crown-4 (*e.g.*, XV)	1.8	1.2[a]–1.5[b]
All 15-crown-5 (*e.g.*, IV)	2.7	1.7–2.2
All 18-crown-6 (*e.g.*, XXVIII)	4.0	2.6–3.2
All 21-crown-7 (*e.g.*, XXXIII)	Over 4	3.4–4.3

[a] According to Corey–Pauling–Koltun atomic models. [b] According to Fisher–Hirschfelder–Taylor atomic models. The ionic diameters of the cations dealt with in this paper are: sodium, 1.90 Å; potassium, 2.66 Å; ammonium, 2.84 Å; rubidium, 2.96 Å; cesium, 3.34 Å; silver, 2.52 Å; and barium, 2.70 Å.

The diameter of the "hole" in XXVIII, the compound with which most of the work had been done, was believed to be 4 Å and this is large enough to accommodate any uncomplexed metal cation. Since the cationic portion of the complexes was thought to be a cyclic polyether with a cation nestling in the center of the hole, it did not seem plausible that a second molecule of the polyether could be involved in complex formation. Hence, the crystalline complexes described in the previous paper[1] were prepared by reacting a mole of polyether with a mole of salt, or with an excess of salt, but never with an excess of polyether. This omission has now been corrected and several new examples of crystalline complexes show that the stoichiometric ratio of polyether to cation can be as high as 2:1.

Results and Discussion

Methods of Preparation of Crystalline Complexes. The complexes were prepared in methanol but, unfortunately, they could not all be prepared under identical conditions. In general, three different methods were used, the first yielding the most reliable results and the third one the least.

Method 1. Different proportions of polyether and salt are reacted in methanol at about 60°, filtered hot, and allowed to stand at room temperature. Crystals that form either on cooling or on the loss of some solvent, but never approaching dryness, are recovered, washed with cold methanol, and dried.

Method 2. A solution of the salt in methanol is mixed with different proportions of a suspension of polyether in methanol and the resulting slurry is stirred at about 60° for 5–10 min. The crystals, after cooling, are recovered as above.

Method 3. Different proportions of polyether and salt are mixed in methanol and the clear solution is allowed to evaporate at room temperature until solids separate, often requiring the removal of almost all the solvent. The crystals, if recovered by filtration, are either not washed with methanol or only sparingly.

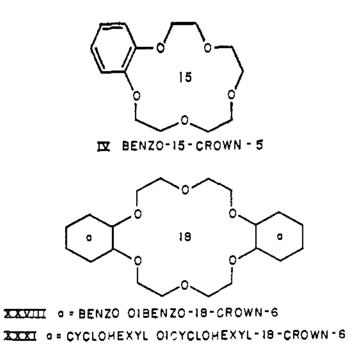

Figure 1. Structural formulas of cyclic polyethers: first number in the name = total number of atoms in the polyether ring; second number in the name = number of oxygen atoms in the polyether ring.

In order to give greater significance to the melting points of the complexes, the melting points of the uncomplexed compounds are listed in Table II.

Table II. Melting Points of Uncomplexed Compounds

Compound	Formula	Mp, °C
Benzo-15-crown-5 (IV)	$C_{14}H_{20}O_5$	79–79.5
Dibenzo-15-crown-5 (XXV)	$C_{18}H_{20}O_5$	113.5–115
Benzo-18-crown-6 (X)	$C_{16}H_{24}O_6$	43–44
Dibenzo-18-crown-6 (XXVIII)	$C_{20}H_{24}O_6$	164
Bis(butylbenzo)-18-crown-6 (XXIX)	$C_{28}H_{40}O_6$	135–137
Dibenzo-21-crown-7 (XXXIII)	$C_{22}H_{28}O_7$	106.5–107.5
Dibenzo-24-crown-8 (XXXV)	$C_{24}H_{32}O_8$	113–114
Dicyclohexyl-18-crown-6 (XXXI) (a mixture of 2 isomers)	$C_{20}H_{36}O_6$	Between 36 and 56
Sodium thiocyanate	NaCNS	287
Potassium thiocyanate	KCNS	173
Ammonium thiocyanate	NH_4CNS	150
Rubidium thiocyanate	RbCNS	188–190
Cesium thiocyanate	CsCNS	204–205
Barium thiocyanate	$Ba(CNS)_2$	Over 290
Silver nitrate	$AgNO_3$	212
Cesium iodide	CsI	621

Results

The compositions and the melting points of the well-defined crystalline complexes and the methods of their preparation are given in Table III.

Except for no. 12, these are considered to be complexes of proven composition and comprise 1:1 and 2:1 complexes. When equal moles of benzo-15-crown-5 and potassium thiocyanate were treated according to method 1, a 38% yield of crystalline 2:1 complex was obtained. Apparently there is no tendency for a 1:1 complex of these components to crystallize out of methanol. When 3 mol of dibenzo-18-crown-6 and 1 mol of cesium thiocyanate were treated according to method 1, unreacted polyether and a 70% yield of crystalline 2:1 complex were obtained, and no evidence was found for the formation of crystalline complexes of a ratio above two polyethers per cation.

Unusual complexes or those with less satisfactory melting point and/or composition are shown in Table IV.

Number 1 is a mixture of benzo-15-crown-5 and its 1:1 complex with sodium thiocyanate, and no. 4 is a mixture of dibenzo-18-crown-6 with its 1:1 complex with potassium thiocyanate.

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(2) B. C. Pressman, Johnson Research Foundation, University of Pennsylvania, Philadelphia, Pa., private communication.

Table III. Well-Defined Crystalline Complexes

			(Mol polyether)/(mol salt)					Calcd, %				Found, %			
No.	Crystalline complex	Method	Reactants	Complex	Mp, °C	Yield, %	Formula	C	H	N	S	C	H	N	S
	Benzo-15-crown-5														
1	NaCNS	1	1:1	1:1	162–165	50	$C_{15}H_{20}NO_5SNa$	51.6	5.7	4.0	9.2	51.5	5.7	4.1	9.5
2	KCNS	2	2:1	2:1	176	77	$C_{29}H_{40}NO_{10}SK$	55.0	6.3	2.2	5.1	55.0	6.0	2.3	5.0
3	NH_4CNS	2	2:1	2:1	131–132	81	$C_{29}H_{44}N_2O_{10}S$	56.9	7.2	4.6	5.2	56.8	7.0	4.5	5.4
4	CsCNS	1	2:1	2:1	127		$C_{29}H_{40}NO_{10}SCs$	47.9	5.5	1.9	4.4	48.0	5.3	2.3	4.8
5	$AgNO_3$	1	2:1	1:1	134–135	59	$C_{14}H_{20}NO_8Ag$	38.3	4.6	3.2	Ag = 24.7	38.3	4.4	3.2	Ag = 24.0
6	$Ba(CNS)_2$	3	2:1	2:1	169–171	17	$C_{30}H_{40}N_2O_{10}S_2Ba$	45.6	5.1	3.5	8.1	45.5	5.1	3.7	8.5
	Dibenzo-15-crown-5														
7	KCNS	3	2:1	2:1	143–144	27	$C_{37}H_{40}NO_{10}SK$	60.9	5.5	1.9	4.4	60.2	5.7	1.8	5.0
	Dibenzo-18-crown-6														
8	KCNS	1	1:1	1:1	245–246	83	$C_{21}H_{24}NO_6SK$	55.1	5.2	3.1	7.0	55.6	4.9	3.2	7.0
9	KCNS	1	2:1	1:1	246–247	33	$C_{21}H_{24}NO_6SK$	55.1	5.2	3.1	7.0	55.6	5.2	3.0	6.6
10	RbCNS	1	1:1	1:1	184–185	>37	$C_{21}H_{24}NO_6SRb$	50.0	4.8	2.8	6.4	50.1	4.6	3.2	6.4
11	RbCNS	1	2:1	2:1	175–176	21	$C_{41}H_{48}NO_{12}SRb$	57.0	5.6	1.6	3.7	56.5	5.4	1.7	3.9
12	CsCNS	1	1:1[a]												
13	CsCNS	1	2:1	2:1	146–147	58	$C_{41}H_{48}NO_{12}SCs$	54.0	5.3	1.5	3.5	53.2	5.3	1.7	3.9
14	CsI	1	2:1	2:1	115–116[b]	53	$C_{40}H_{48}O_{12}ICs$	49.0	4.8	I =	13.0	48.2	5.0	I =	13.0

[a] The spurious 1:1 complex described previously[1] was found to be a mixture of (dibenzo-18-crown-6)$_2$–CsCNS complex mixed with CsCNS. On recrystallization from methanol, 2:1 crystals of satisfactory composition were obtained which melted at 149–150°. All melting points are uncorrected. [b] A portion did not melt even at 270°.

Table IV. Less Well-Defined Crystalline Complexes

			(Mol polyether)/(mol salt)					Calcd, %				Found, %			
No.	Crystalline complex	Method	Reactants	Complex	Mp, °C	Yield, %	Formula	C	H	N	S	C	H	N	S
	Benzo-15-crown-5														
1	NaCNS	3	2:1	2:1	Soft at 80 150–164	38	$C_{29}H_{40}NO_{10}SNa$	56.4	6.5	2.3	5.2	56.9	6.4	2.3	5.7
	Benzo-18-crown-6														
2	KCNS	3	2:1	1:1	112–132	68	$C_{17}H_{24}NO_6SK$	49.9	5.9	3.4	7.8	50.4	5.5	3.6	7.8
3	CsCNS	Special[a]	2:1	3:2	103–104	77	$C_{50}H_{72}N_2O_{18}S_2Cs_2$	45.5	5.5	2.1	4.9	45.2	5.5	2.4	5.3
	Dibenzo-18-crown-6														
4	KCNS	Special[a]	2:1	2:1[b]	164–233	64	$C_{41}H_{48}NO_{12}SK$	60.2	5.9	1.7	3.9	61.6	5.8	1.5	3.5
5	CsCNS	1	1:1	3:2	145–146	85	$C_{62}H_{72}N_2O_{18}S_2Cs_2$	50.9	4.9	1.9	4.4	50.7	5.1	1.9	4.4
	Bis(butylbenzo)-18-crown-6														
6	CsCNS	1	2:1	2:1	108–116	>44	$C_{57}H_{80}NO_{12}SCs$	60.3	7.1	1.2	2.8	59.6	6.7	1.3	3.0
	Dibenzo-21-crown-7														
7	CsCNS	1	2:1	2:1	Soft at 40	*ca.* 20	$C_{45}C_{56}NO_{14}SCs$	54.0	5.6	1.4	3.2	54.1	5.1	1.6	3.2
	Dibenzo-24-crown-8														
8	CsCNS	1	2:1	2:1	88–89	30	$C_{49}H_{64}NO_{16}SCs$	54.1	5.9	1.3	2.9	52.1	5.8	1.6	3.5
	Dicyclohexyl-18-crown-6														
9	KI_3	Special[a]	2:1	1:1	194–195	76	$C_{20}H_{38}O_6I_3K$	30.3	4.6	I = K =	48.1 4.9	30.8	4.6	I = K =	46.0 5.4
10	RbI_3	Special[a]	2:1	1:1	193–195	68	$C_{20}H_{36}O_6I_3Rb$	28.6	4.3	I = Rb =	45.4 10.2	28.6	4.4	I = Rb =	41.5 11.0
11	CsI_3	Special[a]	2:1	3:2	112–114	54	$C_{60}H_{108}O_{18}I_6Cs$	33.6	5.0	I = Cs =	35.5 12.4	33.5	4.9	I = Cs =	34.8 11.5

[a] See the Experimental Section. [b] Pure 1:1 complex crystallized out of the filtrate on standing at room temperature.

Table IV, no. 3, 9, 10, and 11 had to be prepared by evaporating the solutions to dryness and carefully removing the unreacted polyethers without decomposing the complexes with a solvent in which the complexes are not significantly soluble at room temperature.

There are three examples of 3:2 complexes listed in Table IV. Their melting points are sharp and their analyses are acceptable. Their molecular weights were not determined because of probable lack of significance until more is known about the behavior of these complexes in solution in regard to stability and degree of ionization. These complexes will be discussed later.

The powder X-ray diffraction patterns[3] of dibenzo-18-

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(3) We thank J. S. Proctor, Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours and Co., for kindly obtaining the patterns.

crown-6 and the complexes of the following thiocyanates showed that: (1) they are all free of uncomplexed polyether and salt, (2) the patterns of 1:1 potassium, 1:1 and 2:1 rubidium, and 2:1 cesium are distinctly different, but (3) that of 3:2 cesium is basically the same as that of 2:1 cesium except for intensity differences.

The spectrum of dibenzo-18-crown-6 (KBr pellet) obtained with a Perkin-Elmer grating infrared spectrophotometer Model 221 has an absorption band at 10.02 μ. This band is not evident in the spectra of 1:1 complexes of this polyether with sodium, potassium, rubidium, and barium thiocyanates, the 2:1 complexes of cesium thiocyanate and iodide, and the 3:2 complex of cesium thiocyanate. However, the so-called 2:1 complex of potassium thiocyanate (Table IV, no. 4) and the 2:1 complex of rubidium thiocyanate (Table III, no. 11) still show this band, the relative absorbance of the complexes being about 50% of the polyether's.

Discussion

It must be stated at the outset that nothing definitive can be said about the structure of any of these crystalline complexes because single-crystal X-ray analysis has not as yet been successfully applied to this problem. However, sufficient evidence supports the conclusion that the dibenzo-18-crown-6 complexes of the following thiocyanates are of proven composition and integrity: 1:1 potassium, 1:1 and 2:1 rubidium, and 2:1 and 3:2 cesium.

The 2:1 complex of rubidium cannot be a mixture of the 1:1 complex with dibenzo-18-crown-6 because its X-ray pattern does not contain the elements of the polyether pattern. The infrared spectrum of this complex, however, suggests that the two polyether molecules might not be made complex in an identical way.

The 3:2 complex of cesium is an interesting case. The infrared spectrum seems to indicate that the polyether molecules are complexed as in the 2:1 complex, and the similarity of the two X-ray patterns also suggests that the polyether molecules and the cations are arranged in a similar manner.

In the absence of experimental proof of structures, the 2:1 and 3:2 complexes invite speculation concerning them. The cationic portion of the 2:1 complex has a structure consisting, in some way, of (crown)-(cation)-(crown), and that of the 3:2 complex a (crown)-(cation)-(crown)-(cation)-(crown) structure. A "sandwich" structure seems the most probable for the 2:1 complex in which two relatively flat large molecules are held together by a small sphere, particularly when the attractive forces are located on the sphere and toward the centers of the large molecules.

If the 2:1 complexes actually have the "sandwich" structure, they constitute a new group in the class of sandwich compounds previously reported by Taylor, Vergez, and Busch,[4] and by Su and Weiher.[5]

Similarly, the structure of the 3:2 complexes seems most likely to consist of three molecules of polyether arranged flatwise and each separated from the next by a cation. If the term "sandwich" is applicable to the 2:1 complexes, the term "club-sandwich"[6] is an apt one for the 3:2 complexes. Rough approximations of the complexes are depicted in Figure 2.

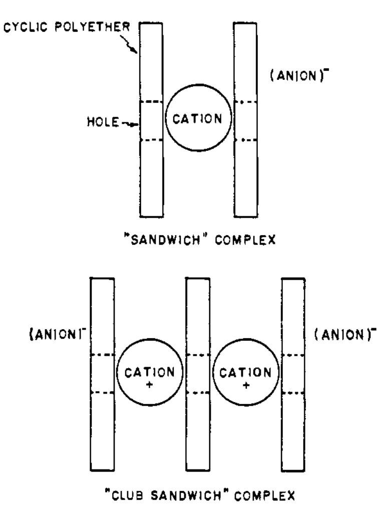

Figure 2. Rough approximations of "sandwich" complexes.

While some physical properties, such as the melting point and X-ray pattern, of a 1:1 complex of a particular cation are likely to differ from those of a 2:1 "sandwich" complex of the same cation, the properties of a 2:1 complex of another cation could be similar to those of a 3:2 "club-sandwich" of the last cation. The former is the case with the rubidium thiocyanate complexes of dibenzo-18-crown-6, and the latter with the complexes of cesium thiocyanate with the same polyether.

The conclusion that the relative sizes of the holes and the cation control the stoichiometry seems inescapable. Dibenzo-18-crown-6 with a hole 2.6–3.2 Å in diameter forms only a 1:1 complex with potassium (diameter, 2.66 Å), but it forms no 1:1 but 2:1 and 3:2 complexes with cesium (3.3 Å), an ion larger than the hole. Rubidium is a borderline case and forms both types of complexes.

By analogy, the complexes of benzo-15-crown-5 can be explained in the same way. This polyether with a hole 1.7–2.2 Å in diameter forms only a 1:1 complex with sodium (1.90 Å), and 2:1 complexes with the larger ions. Why silver (2.52 Å) forms a 1:1 complex is puzzling and indicates that there is more to be known about this matter. A 3:2 complex of benzo-15-crown-5 has not yet been isolated, nor have complexes of dibenzo-18-crown-6 with ratios lying between 1 and 1.5 such as 4:3.

Studies are in progress to determine the thermodynamic properties of solutions of these complexes and to identify the species present in them, but their results will have to await future publication. Cursory experiments, however, in which the crystalline complexes of rubidium thiocyanate with dibenzo-18-crown-6 were put in methylene chloride and in methanol with no additional salt or polyether gave interesting results. The former is a good solvent for the polyether but it does not dissolve the uncomplexed salt, and methanol is a very poor solvent for the polyether but a good one for the salt. The 1:1 complex dissolves in methylene chloride with the precipitation of some uncomplexed salt, showing that the 1:1 complex is, at least partially, converted into the 2:1 cmplex. The 2:1 complex is

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(4) L. T. Taylor, S. C. Vergez, and D. H. Busch, *J. Amer. Chem. Soc.*, **88**, 3170 (1966).

(5) A. C. L. Su and J. F. Weiher, *Inorg. Chem.*, 7, 176 (1968).

(6) First proposed by R. Pariser of this laboratory.

readily soluble in this solvent with no apparent decomposition. On the other hand, the 1:1 complex dissolves in methanol without obvious decomposition, but the 2:1 complex deposits considerable amount of the free polyether, indicating that the 2:1 decomposes into the 1:1 complex in methanol. This behavior must depend on the relative stabilities of the complexes and the solubilities of all the components in the two solvents, and on the coordinating abilities of the solvents.

Other experiments showed that methanol solutions which appear to be stable, upon activation by scratching or filtration, will suddenly begin to deposit large amounts of crystalline complexes. The solubility of the potassium thiocyanate complex of dibenzo-18-crown-6 in methanol given in Table X[1] is exaggerated because of this supersaturation.

By adding to a methanol solution containing potassium and cesium thiocyanates only enough dibenzo-18-crown-6 to form the 1:1 complex of the potassium salt, the two salts were separated almost quantitatively (see Experimental Section).

Experimental Section

The inorganic salts were commercial products and were used after drying in a vacuum oven. The macrocyclic polyethers were prepared according to published methods.[1] The solvents were commercial products and were used without purification. All heating was done on a steam bath and drying in a vacuum oven at 40–60°. Only the unusual preparations and examples of the different preparative methods will be given.

Preparation of (Benzo-15-crown-5)$_1$(NaCNS)$_1$. Table III, No. 1. A mixture of 4.05 g (0.05 mol) of sodium thiocyanate, 22 ml of methanol, and 13.4 g (0.05 mol) of benzo-15-crown-5 (IV) was warmed and the solution was cooled to room temperature. The clear solution was poured into another beaker and seeded with crystals that later formed on the sides of the original beaker. The mass of crystals that formed on standing was stirred apart, filtered, washed with cold methanol, and dried. The crystals weighed 8.8 g, yield 50%.

Preparation of (Benzo-15-crown-5)$_1$(NH$_1$CNS)$_1$. Table III, No. 3. Ammonium thiocyanate, 0.78 g (0.013 mol), was dissolved in 6 ml of methanol and added to a slurry of 5.6 g (0.02 mol) of benzo-15-crown-5 in 10 ml of methanol. Crystals of the polyether began to dissolve but before complete solution, crystals of a different appearance began to form. They were filtered, washed with cold methanol, and dried. A total of 5.0 g of product was obtained, yield 81%.

Preparation of (Benzo-15-crown-5)$_1$(AgNO$_3$)$_1$. Table III, No. 5. A mixture of 1.7 g (0.01 mol) of silver nitrate, 75 ml of methanol, and 5.36 g (0.02 mol) of benzo-15-crown-5 was warmed until a clear solution was obtained. The solution which had turned light brown on standing at room temperature was stirred with 0.2 g of clarifying charcoal, filtered, and allowed to stand shielded from direct light. By the fifth day, some crystals had formed, were isolated (0.1 g) by filtration, and were found to be the uncomplexed polyether. The filtrate suddenly became filled with crystals which were filtered, washed with cold methanol, and dried. The white crystals weighed 2.6 g, yield 59% based on silver nitrate.

Preparation of (Benzo-15-crown-5)$_2$(Ba(CNS)$_2$)$_1$. Table III, No. 6. A mixture of 2.53 g (0.01 mol) of barium thiocyanate, 16 ml of methanol, and 5.36 g (0.02 mol) of benzo-15-crown-5 was stirred until a clear solution was obtained. By the fifth day of evaporation at room temperature, a thick slurry of crystals had formed. It was filtered, washed carefully with a little cold methanol, and dried. The white crystals weighed 1.3 g, yield 17%.

Preparation of (Dibenzo-18-crown-6)$_1$(RbCNS)$_1$. Table III, No. 10. A mixture of 1.233 g (0.0086 mol) of rubidium thiocyanate, 20 ml of methanol, and 3.1 g (0.0086 mol) of dibenzo-18-crown-6 (XXVIII) was warmed until a clear solution was obtained. The solution was concentrated to 14 ml and filtered. On cooling, the filtrate became a mass of crystals which were filtered, washed with cold methanol, and dried. The crystals weighed 1.6 g, yield over 37%. The filtrate was rewarmed and divided into two portions; one was seeded with 1:1 complex crystals and the other with 2:1 crystals, but both gave 1:1 crystals on cooling.

Preparation of (Dibenzo-18-crown-6)$_2$(RbCNS)$_1$. Table III, No. 11. A mixture of 0.98 g (0.0068 mol) of rubidium thiocyanate, 36 ml of methanol, and 4.9 g (0.0068 mol) of dibenzo-18-crown-6 was brought to boiling and the slurry was filtered through a hot filter. The filtrate, 24 ml, did not deposit any crystal on cooling in ice-water and was concentrated to 14 ml. On cooling in ice–water, small crystals began to form very slowly on the bottom of the beaker. They were filtered, washed with cold methanol, and dried. The crystals, 0.46 g, were those of the 2:1 complex. More crystals, 0.8 g, of the same product were recovered from the filtrate after two more days of standing at room temperature; total yield 21%.

In another preparation of the same complex, massive, transparent crystals as large as 4 × 6 mm were obtained.

Preparation of (Dibenzo-18-crown-6)$_2$(CsCNS)$_1$. Table III, No. 13. A mixture of 3.3 g (0.0173 mol) of cesium thiocyanate, 90 ml of methanol, and 12.4 g (0.0344 mol) of dibenzo-18-crown-6 was warmed and filtered hot. The solution was concentrated to 25 ml and filtered hot through coarse paper. The crystals that formed were filtered, washed with cold methanol, and dried. The crystals weighed 9.1 g, yield 58%.

When 1 g of this complex in 30 ml of methanol was boiled, a clear solution was obtained, but on adding 2 g more a copious precipitate of fibrous dibenzo-18-crown-6 formed indicating a partial decomposition of the complex. The filtrate on cooling gave 1.2 g of the 2:1 complex.

Preparation of (Benzo-18-crown-6)$_3$(CsCNS)$_2$. Table IV, No. 3. A mixture of 1.0 g (0.0052 mol) of cesium thiocyanate, 35 ml of methanol, and 3.2 g (0.0103 mol) of benzo-18-crown-6 (X) was warmed and the clear solution was concentrated to 25 ml. No crystals formed immediately, but on the sixth day of evaporation at room temperature, a mass of nearly dry crystals was obtained. It was broken up and dried in a vacuum oven. The white solid, 3.4 g, was completely soluble in methylene chloride but not in benzene. This product (0.4 g) was triturated at room temperature with 10 ml of benzene, filtered, washed with benzene, and dried. The crystals weighed 0.3 g, over-all yield 77%.

Attempted Preparation of (Dibenzo-18-crown-6)$_2$(KCNS)$_1$. Table IV, No. 4. A mixture of 0.97 g (0.01 mol) of potassium thiocyanate, 40 ml of methanol, and 7.2 g (0.02 mol) of dibenzo-18-crown-6 was refluxed for 3 hr while being agitated with a magnetic stirrer. The slurry was filtered hot and the solids were dried without washing. The product, 5.2 g, is the one whose properties are described in Table IV. Its melting range and composition indicate it to be roughly an equimolar mixture of dibenzo-18-crown-6 and its 1:1 complex with potassium thiocyanate. The filtrate, on cooling, gave 1.3 g of pure 1:1 complex, yield 28%.

Preparation of (Dibenzo-18-crown-6)$_3$(CsCNS)$_2$. Table IV, No. 5. A mixture of 1.053 g (0.0055 mol) of cesium thiocyanate, 10 ml of methanol, and 2 g (0.00556 mol) of dibenzo-18-crown-6 was warmed and the resulting clear solution was chilled in ice–water. Some dense crystals (about 0.1 g of impure cesium thiocyanate), that formed on the bottom of the beaker, were recovered by decantation. Crystals began to form at a rapid rate in the mother liquor after about 10 min at room temperature. They were filtered, washed with cold methanol, and dried. The crystals weighed 2.3 g, yield 85%.

Preparation of (Dibenzo-24-crown-8)$_2$(CsCNS)$_1$. Table IV, No. 8. A mixture of 0.468 g (0.00245 mol) of cesium thiocyanate, 12 ml of methanol, and 2.22 g (0.00496 mol) of dibenzo-24-crown-8 (XXXV) was warmed and, on cooling, the clear solution deposited shiny white crystals (0.9 g of nearly pure uncomplexed polyether) which were recovered by filtration. During 5 days at room temperature, crystals formed slowly in the filtrate. They were filtered, washed with cold methanol, and dried. The crystals weighed 0.8 g, yield 30%. The analytical data are very close to the values for the 2:1 complex contaminated with 4% by weight of cesium thiocyanate.

Preparation of (Dicyclohexyl-18-crown-6)$_3$(CsI$_3$)$_2$. Table IV, No. 11. The clear, brown solution obtained by mixing 0.347 g (0.00133 mol) of cesium iodide and 1 g (0.00269 mol) of dicyclohexyl-18-crown-6 (XXXI) in 11 ml of methanol with 0.349 g (0.00133 mol) of iodine dissolved in 14 ml of methylene chloride was evaporated to dryness under vacuum in a rotary evaporator. The brown solids were mixed thoroughly at room temperature with 25 ml of toluene, separated by decantation, and dried. The resulting viscous brown oil solidified on standing at room temperature and weighed 0.77 g, yield 54%.

Table IV, no. 9 and 10 were prepared in the same way but the products did not liquefy during drying.

Competitive Complex Formation. A methanol solution containing 0.97 g (0.01 mol) of potassium thiocyanate and 0.955 g (0.005 mol) of cesium thiocyanate in 20 ml of solvent was prepared by warming. To this solution fibrous crystals of dibenzo-18-crown-6 (3.6 g, 0.01 mol) were gradually added with stirring. The first portion dissolved instantly but when more than half had been added, crystals of a different appearance began to come out. The rest of the polyether and 25 ml of methanol were added and the slurry was warmed and agitated. It was then cooled in ice-water, filtered, washed with cold methanol, and dried. The crystals weighed 3.3 g, yield 72%. The product melted at 244–254° and had the following composition. *Anal.* Calcd for $C_{20}H_{24}O_6$(KCNS): C, 55.1; H, 5.2; N, 3.1; S, 7.0; Cs, nil. Found: C, 55.4; H, 5.0; N, 3.3; S, 7.3; Cs, 1.0.

The filtrate and the methanol washing were combined (total volume 60 ml), added to 3.6 g (0.01 mol) of dibenzo-18-crown-6, and warmed at which nearly all the polyether dissolved. The mixture was filtered hot and allowed to stand at room temperature. Large crystals had formed by the next day, and they were isolated by decantation, washed with cold methanol, and dried. The crystals weighed 2.7 g, yield 59%. The product melted at 145–152° and had the following composition. *Anal.* Calcd for $(C_{20}H_{24}O_6)_2$(CsCNS): C, 54.0; H, 5.3; N, 1.5; S, 3.5; K, nil. Found: C, 53.9; H, 5.0; N, 1.7; S, 3.6; K, 0.03.

The first crystals to come out are those of the 1:1 complex of potassium thiocyanate contaminated with some cesium compound. This would seem to indicate that this complex is more stable than the 2:1 complex of cesium thiocyanate which is formed subsequently. Although this conclusion is probably correct, the relative solubilities of the two complexes in methanol must also be involved.

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New Macrocyclic Polyethers

C. J. Pedersen

Contribution No. 212 from E. I. du Pont de Nemours & Company, Inc.,
Elastomer Chemicals Department, Experimental Station,
Wilmington, Delaware 19898. Received May 22, 1969

Abstract: Nine new macrocyclic polyethers have been synthesized including acetals, a carbonate, and a derivative of 1,8-dihydroxynaphthalene. Dicyclohexyl-15-crown-5 is the best complexing agent for Na^+ found to date, and dicyclohexyl-16-crown-5 the most specific for Na^+ *vs.* the other alkali cations. The acetal polyethers are less effective complexing agents than similar compounds in which $-OCH_2O-$ has been replaced by $-OCH_2CH_2O-$.

The preparation and properties of a number of macrocyclic polyethers derived from aromatic vicinal diols have been previously reported.[1] It was shown that certain of these compounds, particularly those containing five to ten oxygen atoms, form stable complexes with the alkali and alkaline earth cations, and that the most favorable linkage for complexation is $-OCH_2CH_2O-$, followed by $-O(CH_2)_3O-$ and becoming ineffective beyond $-O(CH_2)_4O-$, but the effect of $-OCH_2O-$ had not been determined. It was further demonstrated that saturated compounds are better complexing agents than the corresponding aromatic compounds from which they are obtained by catalytic hydrogenation. The dibenzo polyethers containing five oxygen atoms were found to have a special affinity for the sodium ion, but they had not yet been hydrogenated to improve their effectiveness.

In a continuation of this work, nine new macrocyclic polyethers were synthesized: three contain the $-O-CH_2-O-$ link to test the effect of this group on complex formation; two are saturated compounds derived from dibenzo-5-oxygen compounds; one is a product obtained from a dibenzo compound by hydrogenating only one of the atomatic rings; one is a derivative of 1,-8-dihydroxynaphthalene which is not a vicinal diol; and two were prepared by ring-closing 1,17-dihydroxy-4,5,:13,14-dibenzo-3,6,9,12,15-pentaoxaheptadeca-4,13-diene, an intermediate which is well adapted to this process.

The code numbers and the structural formulas of the new compounds are shown in Figure 1. The digits within the diagrams indicate the total number of atoms in the polyether ring. The code numbers continue the series started in the original paper,[1] and the abbreviated nomenclature described therein will be used whenever applicable without ambiguity; otherwise, the compounds will be identified by their code numbers. L is dicyclohexyl-15-crown-5, LI is dicyclohexyl-16-crown-5, LII is benzocyclohexyl-18-crown-6, and LVIII is 1,8-naphthyl-16-crown-5; the others cannot be named in this way without using too many numbers. The full names of all these compounds are given in the Experimental Section. LVI is a cyclic polyether and a carbonate, but it is included here because it might be considered derived from LIV by the oxidation of the methylene to the carbonyl group. XXI is dibenzo-16-crown-5, XXV is dibenzo-15-crown-5, XXVIII is dibenzo-18-crown-6, and XXXI is dicyclohexyl-18-crown-6. The first three are mentioned in Table I and the last in Table IV. The structures of these compounds are shown in the original reference[1] but they should be discernible from their abbreviated names.

Results and Discussion

The methods used for and other information pertinent to the synthesis of these polyethers are shown in Table I, the melting points and the analytical data are given in Table II, and the ultraviolet spectra are summarized in Table III. Note that LIII, LIV, and LVII contain at

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(1) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).