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STOICHIOMETRIC ALKALINE EARTH SALT COMPLEXES OF OLIGOETHYLENE GLYCOLS

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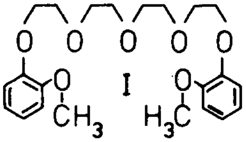
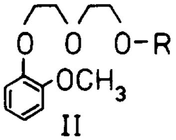
Oligoethylene glycol ethers, I, with rigid donor end groups give in analogy to cyclic crown ethers crystalline complexes with salts of alkali and alkaline earth metals as well as with neutral molecules [1)]. In a series of cases the cation is helically encircled by the open-chain crown ether [2)]. We recently found that oligoethers of the types II-IV containing certain structural units are also able to form crystalline complexes with cations from the 1. and 2. main groups of the Periodic Table [3)].


I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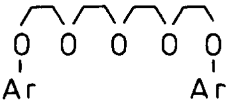
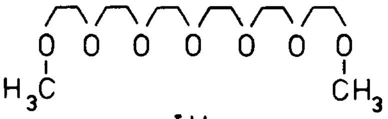
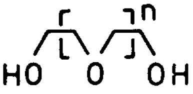
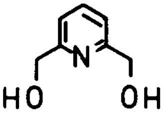

III Ar = Aryl


IV

According to ^{23}Na- [4)] as well as UV-measurements [5)], 1,2-ethanediol is a more effective donor system than diglyme resp. triglyme and we therefore examined the ability of simple glycols to form crystalline alkali and alkaline earth metal salt complexes[6)].


V


VI-IX


X


XI

We have now obtained the first stoichiometric crystalline complexes of glycols V-XI with alkaline earth metal salts (data see table 1). It is remarkable that even glycols with only 3 donor atoms like diethylene glycol still form 1:1 complexes with the relatively large Ba^{2+} ions. The 2:1 stoichiometry in the diethylene glycol·$Ca(SCN)_2$ -complex also indicates a complex structure different from the usual open-chain type. This also seems to be true for the 1:1 complex of 1,2-ethanediol (V) with $Ba(SCN)_2$. For the 2:1 complex of pyridine-2,6-dimethanediol (X) with $Ba(SCN)_2$ a clasp of the cation by two vertically oriented pyridine units is reasonable.

Spectroscopic results show that no (acidic) salts [7)] of the glycols are formed, but that the complexes exhibit crown ether complex properties. IR spectra and elemental analyses confirm the presence of $SCN^{\ominus}$ in the thiocyanate complexes. Because of the

Table 1. Synthesized complexes of glycols V-XI [8]

Ligand No.	$\underline{\underline{n}}$	Salt used	complexes: mp [°C] (solvent)	stoichiometry ligand : salt	analyses	C	H	N
V		$Ba(SCN)_2$	84 (dec.) (ethylacetate/petroleum ether)	1:1	calcd.:	15.22	1.91	8.88
					found :	14.93	1.82	9.00
VI	1	$Ca(SCN)_2$	162 (ethylacetate/petroleum ether)	2:1	calcd.:	32.59	5.47	7.60
					found :	32.45	5.39	7.63
		$Ba(SCN)_2$	142 (dec.) (ethylacetate/methanol)	1:1	calcd.:	20.03	2.80	7.78
					found :	20.03	2.92	7.80
VII	2	$Ba(SCN)_2$	198 (dec.) (trichloromethane/methanol)	1:1	calcd.:	23.80	3.49	6.93
					found :	24.01	3.39	6.91
VIII	3	$Ca(SCN)_2$	160 (dec.) (ethylacetate/methanol)	1:1	calcd.:	34.27	5.17	7.99
					found :	34.57	5.19	8.09
IX	4	$Ca(SCN)_2$	190-200 (dec.) (ethylacetate/methanol)	1:1	calcd.:	36.53	5.62	7.10
					found :	36.67	5.67	6.88
		$Ba(SCN)_2$	157 (dec.) (ethylacetate/methanol)	1:1	calcd.:	29.30	4.50	5.69
					found :	29.57	4.42	5.71
X		$Ba(SCN)_2$	171 (ethylacetate/methanol)	2:1	calcd.:	36.13	3.41	10.53
					found :	36.05	3.41	10.48
XI		$Ca(SCN)_2$	173 (ethylacetate/methanol)	2:1	calcd.:	36.34	6.10	7.06
					found.:	36.45	6.17	7.33

lower solubility of the glycol complexes, particularly in comparison to the complexes of the aryl ethers I-III, no definite chemical shifts (^1H-NMR) of the CH_2-protons relative to the free ligands can be observed in the required polar solvents.

The stereochemistry of the crystalline complexes is a subject for x-ray structure elucidation and it could be the key for a better understanding of complex formation by polyhydroxy compounds [9] like inositols, sugars etc.

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8) We would like to thank Dr.*W.Ochterbeck,* Mrs.*J.Schütz* and Mrs.*A.Scholz* for the elemental analyses; Dr.*G.Eckhardt* for the mass spectra and Mr.*F.Schmitt* for experimental collaboration; Mr.*Ph.Koo Tze Mew* for his helpful advice in the translation of the manuscript.

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