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Polyoxalactones and Their Cationic Complexes

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SUMMARY

Some polyoxalactones were synthesised from the dichlorides of glycolic acids and polyethyleneglycoles in the presence of pyridine. The polyoxalactones were also complexed with some of alkaline and alkaline earth salts and quite stable polyoxalactone-salt complexes were obtained including the Ca^{++} cation. Complexes obtained exhibited mostly 1:1 type of complex stoichiometry regardles from radius of the cation and the nature of lactone ring.

INTRODUCTION

Polyoxalactones of macrocyclic compounds have received very much attention after quite a number of reports on macro cyclic ethers as multidendate ligands binding most cations, resembling the naturally occurring macrocyclic antibiotics(1,2). Among the methods to be tried we found the cyclic ester formation from diacid chlorides and the polyglycoles rather convenient particularly due to the formation of negligible amount of polymeric side products(3,4).

Complexing ability of such compounds has already been tried in methanol by some authors and their significant effect of cation binding was explained(4,5).

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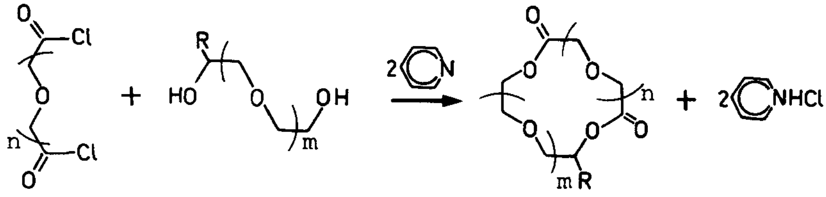
RESULTS

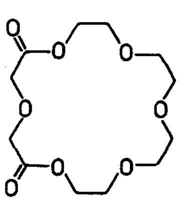
We have prepared the some of the polyoxalactones as it is discribed in our previous study (4). In this procedure polyoxalactone ring was formed by condensing the dichlorides of glycolic acids (5) with polyglycoles in the presence of equivalent amount of pyridine in dry benzene solutions under nitrogen. We have also synthesised a chlormethyl derivative of pentoxacyclopentadecane -2,6-dione as a substituted form of the lactones (II.B.)(6).



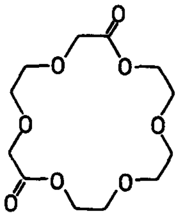
IA (n:0 m:2 R:H)
IIA (n:0 m:3 R:H)
IB (n:1 m:2 R:H)
IIB (n:1 m:2 R:CH_2Cl)
IIIB (n:1 m:3 R:H)
IC (n:2 m:2 R:H)
IIC (n:2 m:3 R:H)

(IA - IIC)

Some of the lactones gave quite stable salt complexes. We could therefore obtaine some alkaline and alkaline earth lactone-salt complexes of 1,4,7,10,13,16-hexaoxacyclooctadecane-2,6-dione and 1,4,7,10,13,16-hexaoxacyclooctadecane-2,9-dione (III.B and I.C) in partly hydrated forms. However in the present study we just particularly selected the salts of large anions providing the higher stability. Table-I,II.



IIIB



IC

Table I. SOME POLYOXALACTONES.

	n	m		M.P. (°C)	B.P. (°C)	Yield (%)
I A	0	2	1,4,7,10-tetraoxacyclododecane-2,3-dione	59	--	70-75
II A	0	3	1,4,7,10,13-pentaoxacyclopentadecane-2,3-dione	84	--	75-80
I B	1	2	1,4,7,10,13-pentaoxacyclopentadecane-2,6-dione	98	--	80-85
II B	1	2	1,4,7,10,13-pentaoxa-15-chlormethylcyclopentadecane-2,6-dione	86	--	80-85
III B	1	3	1,4,7,10,13,16-hexaoxacyclooctadecane-2,6-dione	79	--	35-40
I C	2	2	1,4,7,10,13,16-hexaoxacyclooctadecane-2,9-dione	(x)	180/0,02	40-45
II C	2	3	1,4,7,10,13,16,19-heptaoxacycloheneicosane-2,9-dione	oil	210/0,02	35-45

(x) Hygroscopic.

Table II. Some Complexes of 1,4,7,10,13,16-hexaoxacyclooctadecane-2,6-dione (III.B).

Salt	Structure	M.W.	M.P. (^{o}C)	Yield (%)	Ratio M :II.C:H_2O	% Calc. C	% Calc. H	% Found[(c)] C	% Found[(c)] H
$NaClO_4.H_2O$	$C_{12}H_{20}O_{12}ClNa$	414,73	206-212	65	1:1	34,72	4,82	35,57	4,75
$KClO_4$	$C_{12}H_{20}O_{12}ClK$	430,84	202-203	45	1:1	33,42	4,64	31,65	3,73
KSCN	$C_{13}H_{20}NO_8SK$	389,47	169-170	42	1:1	40,05	5,14	40,29	5,16
$Ca(ClO_4)_2.4H_2O$	$C_{24}H_{46}O_{35}Cl_4Ca_2$ (a)	1116,60	115-120	42	2:2:3	25,79	4,12	25,18	4,41
$Sr(ClO_4)_2.4H_2O$	$C_{12}H_{20}O_{16}Cl_2Sr$	578,81	270 (b)	64	1:1	24,88	3,46	25,04	3,53
$Ba(ClO_4)_2.3H_2O$	$C_{12}H_{20}O_{16}Cl_2Ba$	628,53	275 (b)	76	1:1	22,91	3,18	23,08	3,25
$Pb(ClO_4)_2.3H_2O$	$C_{12}H_{20}O_{16}Cl_2Pb$	698,37	253 (b)	47	1:1	20,62	2,86	20,62	2,86 (d)

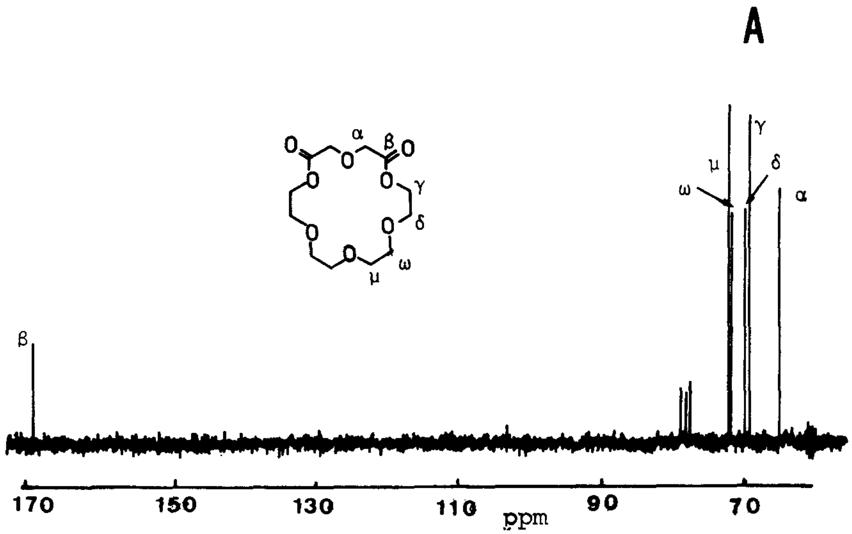
(a) Hygroscopic. (b) Decomposition temp. (c) C.H analyses were performed after 100°C/0,02 mBar drying.

(d) Determined by Atomic Absorption.

Table III. Some Complexes of 1,4,7,10,13,16-hexaoxacyclooctadecane-2,9-dione (I.C).

Salt	Structure	M.W.	M.P. (°C)	Yield (%)	Ratio M^+:III.B:H_2O	% Calc. C	% Calc. H	% Found[(c)] C	% Found[(c)] H
$NaClO_4 \cdot H_2O$	$C_{12}H_{20}O_{12}ClNa$	414,73	210-212	14	1:1	34,72	4,82	32,82	4,97
$KClO_4$	$C_{12}H_{20}O_{16}Cl_2K_2$ (a)	569,39	201-202	17	2:1	25,29	3,51	25,53	3,66
KSCN	$C_{13}H_{20}NO_8SK$	389,47	182-183	12	1:1	40,05	5,14	40,05	4,97
$Ca(ClO_4)_2 \cdot 4H_2O$	$C_{24}H_{46}O_{35}Cl_4Ca_2$	1116,60	247 (b)	2	2:2:3	25,79	4,12	26,56	4,92
$Sr(ClO_4)_2 \cdot 4H_2O$	$C_{12}H_{20}O_{16}Cl_2Sr$	578,81	270 (b)	9	1:1	24,88	3,46	25,07	3,50

(a) Hygroscopic. (b) Decomposition temp. (c) C.H analyses were performed after 100°C/0,02 mBar drying , determinations were carried out by Analytische Laboratorien, Dr.H.Malissa-G.Reuter,Engelskirchen, Germany.



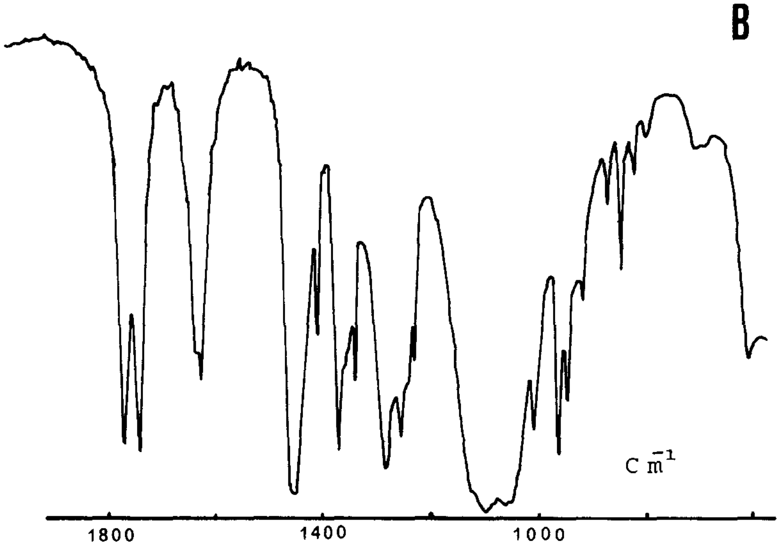


Figure-1.A 50,29 MHz ^{13}C nmr spectrum of 1,4,7,10,13,16-hexaoxacyclooctadecane-2,6-dione (III.B.) in $CDCl_3$

Figure-1.B. Partial IR spectrum of $CaCl_2.4H_2O$ complex of 1,4,7,10,13,16-hexaoxacyclooctadecane-2,6-dione(III.B.) as nujol muls.

IR spectra of complexes exhibited the streching carbonyl bond around 1740 cm^{-1} indicating the planar arrangement around the cation as it was claimed by some of the authors(1). However $Ca(ClO_4)_2$.IIIB.$4H_2O$ complex displayed a splitting around the 1740 and 1770 cm^{-1} (Figure-1B) although such a result could simply be explained by the behavior of smaller size of lactone-ether rings(7,8). On the other hand a stable Ca^{++} Complex is the first reported result for a hexaoxa ring compound(Table-II) even for 18-Crown-6 although Boer (9) has reported that the 12-Crown-4 formed a solid complex with Ca^{++}. It is an important result which contributes for clarifying novel role of the Ca^{++} ion in Biology.

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