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Neutral acyclic analogues of crown-ethers and cryptands and their complex-forming properties

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ABSTRACT. **The review deals with neutral podands (acrylic analogues of crown ethers) of various types, their structures, their complex-forming properties, and their practical applications. Phosphorus-containing and analogous organoelement podands are not included in the review.**

The bibliography incorporates 241 references.

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I. Introduction

The term "podands" appeared in the chemical literature comparatively recently — towards the end of the 1970s.[1,2] It embraces various types of acyclic polyether complex-forming agents. The name comes from the Greek word "podos" — foot. In the podand molecule, there is one or several "feet" formed by polyether chains with various end groups. According to the number of such feet, podands are divided into mono-, di-, tri-, and poly-podands. Compounds of this type can be investigated long before the appearance of the term "podands" itself. Thus the simplest representatives of monopodands [diethyl ethers of oligo(ethylene glycols — glymes] became well known in the 1950s–1960s as solvents solvating alkali and certain other metal cations.[3,4] Polyether acyclic antibiotics (nigericin, monensin, etc.), containing tetrahydrofuran and tetrahydropyran rings in the chain, which were discovered and vigorously investigated in the 1950s–1970s, belong to the same type of complex-forming agents.[5] These compounds effect the transport of alkali metals through artificial and biological membranes. In the complex formation reaction, the molecules of acyclic antibiotics twist round a cation and form a pseudoring stabilised by the intramolecular interaction of the end groups.

The specific synthesis of podands as a special class of ligands began to develop mainly after Pedersen's discovery in 1967 of the complex-forming properties of crown ethers.[6] Oligo- and poly-(ethylene glycols) and glymes began to be regarded as open-chain analogues of crown ethers. Polydentate acyclic complex-forming agents of a new type were created on their basis[1] and found extensive application as solvents. Despite certain advances, this field nevertheless remained of secondary importance compared with the much more thoroughly developed and popular field of macrocyclic complex-forming agents.[7,8] However, in recent years open-chain analogues of crown-ethers have attracted increasing attention because of their availability, fairly high effectiveness, and the possibility of regulating on a wide scale their complex-forming properties by altering their structure. Their properties as phase-transfer catalysts,[9–12] extractants,[13,14] and as components of ion-selective electrodes[15] are being investigated. The growing interest in this new class of complex-forming agents is reflected by review articles[1,16,17] on this topic.

The present review differs from those already published by a much more complete coverage of literature (up to 1988), an attempt at the analysis of the dependence of the complex-forming capacity of podands on their structure, and a discussion of the applied aspects of the problem.

II. Neutral acyclic unbranched ligands — monopodands

1. Introduction

The specific solvation of alkali and alkaline earth metal cations by ethylene glycol ethers and their oligomers (glymes) is well known.[3,4] The use of these compounds as solvents for organic anionic reactions is in fact based on this phenomenon. Diglyme, which is in essence a fragment of the 18-crown-6 ether molecule, has come to be widely used. Following the discovery of crown-ethers in the second half of the 1960s, chemists again turn their attention to oligo(ethylene glycols) and glymes as cheaper analogues and began to investigate vigorously their complex-forming properties relative to those of crown-ethers.[18–21]

The principal method of synthesis of monopodands having the general formula $RO(CH_2CH_2O)_nR$ with various end groups is the Williamson reaction between the corresponding dihalides and hydroxyl-containing compounds in the presence of a base.[1]

Individual oligo- and poly-(ethylene-glycols) are obtained as a rule[22] by the reaction of the monoalkoxide of the lowest oligo-(ethylene glycol) with the dihalide of the corresponding oligo(ethylene glycol) using alkali metals or their hydroxides as metallating agents. The alkoxide of the lowest glycols was synthesised using sodium hydroxide, distilling away the water formed as a result of the reaction.[23] The yields of poly(ethylene glycols) do not then exceed 60%.

Ethers of oligo(poly)(ethylene glycol) were obtained by alkylating the corresponding alkali metal glycosides with a 1.5–3.0-fold excess of the alkyl halide at 50–90 °C in a solvent or in its absence. They

are freed from salts by filtration or with the aid of ion-exchange resins.[24]

The formation constants of the complexes of podands with metal cations are determined by NMR, IR, and UV spectroscopy, calorimetry, conductimetry, potentiometry, and extraction methods.

2. Oligo(poly)(ethylene glycols) and glymes

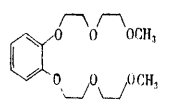
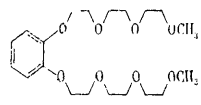
The formation of complexes by poly(ethylene glycols) (in which the number of units is $n = 1-8$) with alkaline and alkaline earth metal cations in aprotic solvents has been observed by the NMR method.[25] The formation constants of the complexes of glymes with alkali metal picrates in toluene were measured spectrophotometrically and were compared with data for crown-ethers.[26]

Oligo- and poly-(ethylene glycols) exhibit a fairly strong capacity for ion–dipole interaction with alkali and alkaline earth metal cations in methanol, which is a polar proton-donating solvent.[27–35] The interaction is in general determined by the ionic radius of the cation and the number of glycol units. The relatively strong interaction with large cations is due to the flexibility of the glycol molecule, which is able to assume the energetically favourable *trans*, *gauche*, *trans*-conformation.[36,37] The weak interaction with lithium and sodium cations has been explained[30] by the vigorous solvation of the latter by methanol. However, there exist conductimetric data[38] according to which glycols with $n = 2-4$ form fairly stable complexes with lithium picrate in isopropyl alcohol. Their composition corresponds to metal : ligand = 1 : 2 and their stability constants are approximately the same ($\lg K_{st} \simeq 2.37-2.51$). It has been shown[39] that in an aprotic solvent (toluene) the lower glycols with $n = 2-4$ are also capable of dissolving alkali and alkaline earth metal mono-, di- and tri-nitrophenoxides. According to NMR data,[28,40] the optimum number of units in the oligo(ethylene glycol) is six in the interaction with sodium and calcium cations, seven in the interaction with potassium, rubidium, caesium, and strontium cations, and five–seven for the barium cation. Glymes having the same number of binding sites as a rule interact somewhat more weakly with sodium and calcium cations in methanol, whereas the monomethyl ethers of the corresponding glycols occupy an intermediate position[28,32] (Table 1). On the other hand, it has been shown for a large series of poly(ethylene glycols) and their mono- and di-methyl ethers by the potentiometric method that,[31,32] with increase in the length of the polyether chain, the stability of the complexes of these ligands with the sodium cations increases (Table 1). Neither maxima, nor the attainment of a plateau, nor a decrease in complex-forming capacity were observed under these conditions. The complex formation constants for poly(ethylene glycols) and their derivatives with molecular weights in the range 1000–14 000 ($n = 24-319$) are closer to those for 15-crown-5- and 18-crown-6-ethers. The stability of the sodium complexes on poly(ethylene glycols) and their ethers with a lower molecular weight is lower by 2–3 orders of magnitude than the stability of the complexes of the above macrocyclic compounds.[32,41] The replacement of two methyl end groups by the $C_2H_5OCOCH_2CH_2$ groups has little effect on the complex formation constants. The replacement of the central ethylene glycol unit by the rigid catechol unit is hardly reflected in the complex-forming properties of glymes[27,42] (Table 1). Poly(ethylene glycols) with a 1,2-acenaphthene fragment[43] and glymes with a central ferrocene nucleus[44] are known.

The stability constants of the lanthanide complexes of tetraglyme in propylene carbonate have been determined potentiometrically.[45] The stability of these complexes ($\lg K_{st} = 5.05$) proved to be lower by 1.5 orders of magnitude than in the case of 15-crown-5-ether and higher by an order of magnitude than for the complex of 3-t-butylbenzo-15-crown-5-ethyl.

Not only association with metal cations in solutions but also the formation of crystalline complexes is characteristic of oligo(ethylene glycols) and their dimethyl ethers. Numerous studies have been devoted to the synthesis and crystal structures of the complexes of glymes with transition metal salts.[1] According to the principles of hard and soft acids and bases, the most stable complexes are formed with transition metal cations by analogues of glymes with nitrogen or sulphur atoms or their combinations.[46–54] Crystalline complexes of oligo(ethylene glycols) and their derivatives with lanthanide nitrates and perchlorates have been obtained.[55,56]

Table 1. The logarithms of the stability constants of complexes of poly(ethylene glycol) ligands $R^1O(CH_2CH_2)_nR^2$, certain other ligands, and macrocycles with alkali metal halides in methanol.

n	R^1	R^2	$\lg K_{st}$			Refs.
			$Na^+(Cl^-)$	$K^+(I^-)$	$Cs^+(Cl^-)$	
4	H	H	1.64	—	—	[32]
4	CH_3	CH_3	1.28	1.72	1.45	[27]
4	CH_3	CH_3	1.44	1.59	1.43	[33]
5	H	H	—	2.01	1.29	[33]
5	H	CH_3	—	1.98	1.68	[33]
5	CH_3	CH_3	1.47	2.20	1.85	[27]
5	CH_3	CH_3	1.54	2.07	1.76	[33]
6	H	H	2.02	3.05	1.67	[32, 33]
6	CH_3	CH_3	1.60	2.55	2.17	[27]
6	CH_3	CH_3	1.56	2.55	2.10	[33]
7	H	CH_3	1.82	—	—	[32]
7	CH_3	CH_3	1.67	2.87	2.41	[27]
24	H	H	2.88	—	—	[32]
24	CH_3	CH_3	2.55	—	—	[32]
183	H	H	3.70	—	—	[32]
319	H	H	4.08	—	—	[32]
4	$CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$	$CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$	1.25	1.89	1.60	[27]
4	$CH_2CH_2\overset{\overset{O}{\|}}{C}OC_2H_5$	$CH_2CH_2\overset{\overset{O}{\|}}{C}OC_2H_5$	1.34	1.78	1.56	[27]
			1.44	2.15	1.66	[27]
			1.61	2.83	2.29	[27]
	15-Crown-5		3.25	—	—	[32]
	18-Crown-6		4.35	6.10	4.62	[32, 41]

Crystalline complexes of glymes with alkali and alkaline earth metal cations could not be obtained for a long time.[6,57] However, numerous crystalline complexes of not only glymes but also glycols

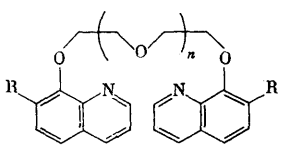
with alkali and alkaline earth metal salts are now known.[25,8-61] These complexes form stoichiometric complexes. They have been synthesised mainly from metal thiocyanates. The interaction of oligo(ethylene glycol) with cations is of the donor–acceptor type and resembles the formation of complexes by macrocyclic polyethers.[6] The structures of certain complexes of oligo(ethylene glycol) have been established by X-ray diffraction.[62-64]

Thus oligo(poly)(ethylene glycol) and their alkyl ethers exhibit complex-forming properties in relation to alkali, alkaline earth, transition, and other metal cations. However, in terms of their complex-forming capacities, these compounds are largely appreciably inferior to macrocyclic polyethers. Only poly(ethylene glycol) and their alkyl ethers with a high molecular weight approach crown-ethers as regards effectiveness.

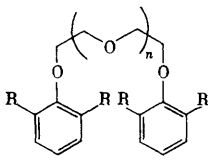
3. Monopodands with rigid end groups

As shown above, only poly(ethylene glycols) with a high molecular weight can to some extent compete with crown ethers (Table 1). According to the concept of end groups proposed by Vögtle,[65] the introduction of aromatic substituents carrying electron-donating centres at the ends of the oligo(ethylene glycol) chain greatly facilitates complex formation. The electron-donating centres of rigid end groups fix the metal cation in the complex formation reaction. The entire ligand molecule can then assume the conformation ensuring the coordination of the electron-donating centres incorporated in the oligo(ethylene glycol) chain. Vögtle and co-workers synthesised in the 1970s a wide variety of aromatic analogues of oligo(ethylene glycol)ethers with rigid groups at one or both ends of the polyether chain.[1] These studies in fact initiated a new stage in the development of podands. There was a transition from solvating solvents to solid complex-forming agents used as solvating additives.

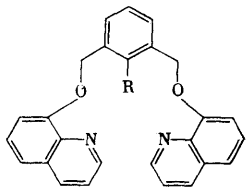
The first representatives of compounds of this type were bis(quinolinyl)oligo-ethers having 8-hydroxyquinoline residues at the ends of the oligo(ethylene glycol) chain structure (I).



(I), $n = 1 \div 6$
$R = H, CH_3$



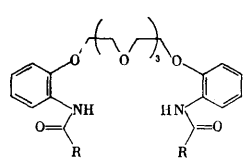
(II), $n = 1 \div 3$
(III), $n = 0 \div 2$



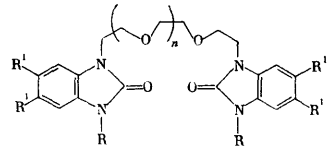
(IV), $R = H, OCH_3, NO_2$

The phenyl, *o*-hydroxy-, *o*-methoxy-, *o*-nitro-, and *o*-ethoxy-carbonyl-phenyl groups [compounds (II)] and the 2,6-dimethoxy-phenyl group [compound (III)] can be used as rigid end groups.[1,42] The flexible glycol units in ligand molecules can be replaced by rigid aromatic units [as in compound (IV)].[57]

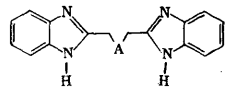
Monopodands with amidophenyl [compound (V)], benzimidazole [compounds (VI) and (VII)], and substituted thiadiazole end groups are known.[65-69] In order to create ligands capable of "becoming adjusted" to various ions, oligo(ethylene glycols) (V), in which R represents a polyether residue with the *o*-nitrophenyl group at the end, were synthesised.[70]



(V)



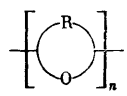
(VI)



(VII)

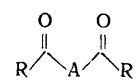
(VI), $n = 0, 1$; $R = R^1 = H, CH_3$;
$R = CH_2CO_2C_2H_5$, $C(CH_3)=CH_2$; (VII),
$A = O, OCH_2CH_2O, S, CH_2SCH_2, 1,2\text{-}OC_6H_4O$.

Podands of a special type were constructed exclusively from cyclooxaalkane segments.[71] Some of these ligands bind metal cations in the same way as crown-ethers, but, in contrast to the latter, they form complexes with a large set of cations.



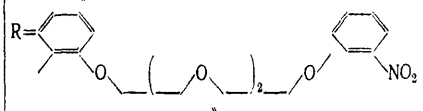
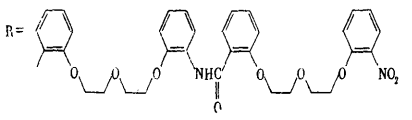
The cation-binding properties of these ligands are manifested particularly clearly when the average length of the segment is sufficient ($n = 6$) and the cyclic units have the *threo*-configuration. Nevertheless, in an experiment on the transport of lithium and potassium picrates from an aqueous solution to chloroform, 18-crown-6 was more effective (63.74%) than the ligand and six tetrahydrofuran units (37.53%) (the amount of the transferred lithium and potassium salt respectively is indicated in brackets).

Ligands with ester groups [compound (VIII)] have been attained by treating alcohols, phenols, and oligo(ethylene glycols) with benzyl chloride, phenylacetyl chloride, or *o*-phenylenedioxydiacetyl chloride.[1,16,72-74]



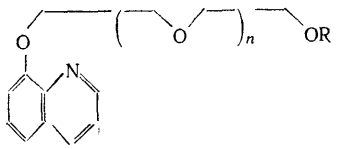
(VIII), $A = (OCH_2CH_2)_nO$, $(n = 1 \div 5)$; CH_2OCH_2; $o\text{-}CH_2OC_6H_4OCH_2$;
$R = OC_4H_9$, $(OCH_2CH_2)_2OC_4H_9$, $2\text{-}R^1C_6H_4$ ($R^1 = H, OCH_3, NO_2$),
$3.5\text{-}(NO_2)_2C_6H_3$, $2.5\text{-}(CH_3)_2C_6H_3CH_2$

Table 2. The logarithms of the stability constants of complexes of monopodands with alkali and alkaline earth metal salts.

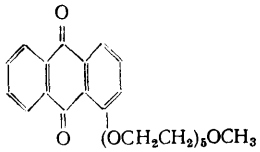
No. of compound	Structure	$\lg K_{st}$								Solvent	Method	Refs.
		Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}			
(I)	$n=3$, R = H	2.37	3.22	3.51	3.06	2.6	4.99	—	3.87	CH_3OH	A	[33, 75]
(IIa)	$n=3$, R = R^1 = H	<0	0.7	1.58	0.5	<0	—	—	—	»	"	[75]
(IIb)	$n=3$, R = H, $R^1 = NO_2$	<1	1.43	1.59	1.93	1.75	—	—	—	»	"	[75]
(V)	$R = CH_3$	—	1.85	—	—	—	—	—	—	C_5H_5N	B	[85]
(V)	»	—	1.53	—	—	—	—	—	—	CH_3CN	"	[70]
(V)		—	2.25	—	—	—	—	—	—	C_5H_5N	"	[85]
(V)	»	—	1.07	—	—	—	—	—	—	CH_3CN	"	[70]
(V)		—	1.90	—	—	—	—	—	—	C_5H_5N	"	[85]
(IX)	$n=3$, R = Ph	<0.7	1.51	1.87	1.79	1.58	—	—	—	CH_3OH	A	[75]
(XIV)	$n=0$, X = O, R = R^2 = CH_3, $R^1 = (CH_2)_{11}OC(O)C_2H_5$	1.9	2.1	1.8	1.9	—	3.0	3.3	4.4	C_2H_5OH	C	[86]
(XIV)	$n=0$, X = O, R = H, R^1 = R^2 = Ph	<1.2	2.4	2.2	2.1	—	2.4	2.9	4.0	»	"	[86]
(XIX)	A = o-C_6H_4, R = R^1 = C_3H_7	1.8	1.0	—	—	—	—	—	—	CH_3OH	A	[75]
(XXVIII)	$m=2$, R = R^2 = CH_3, $R^1 = C_7H_{15}$	5—6	—	—	—	—	—	—	—	CH_3NO_2	B	[87]
(XXVIII)	»	3	—	—	—	—	—	—	—	CH_3CN	"	[87]
(XXVIII)	»	1.1	—	—	—	—	—	—	—	C_5H_5N	"	[87]
—	Nigericin	—	4.0	5.7	—	—	—	—	—	CH_3OH	C	[41]
—	18-Crown-6	—	4.3	6.1	—	4.6	—	—	—	»	"	[41]

Note. A = spectrophotometry, B = NMR spectroscopy, and C = potentiometry.

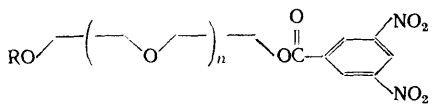
The asymmetric compounds (IX) and (X), containing a combination of different end groups, sometimes a combination of strongly and weakly electron-donating residues, have been synthesised.[42,65,75–79]



(IX), $n=1-3$, R = H, CH_3, Ph, 2-CH_3O-4-$CH_3C(O)C_6H_3$, 2-$R^1C_6H_4$ ($R^1 = OCH_3$, CN); 1-naphthyl.



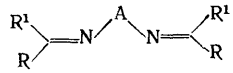
(X)



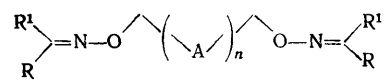
(XI), $n=2-4$, R = Ph, 2-$CH_3OC_6H_4$, 4-$CH_3OC_6H_4$, 3,5-$(CH_3O)_2C_6H_3$, 1-naphthyl

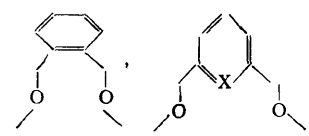
The polyethers (XI), in which electron-donating and electron-accepting groups at the ends of the chains are combined, have been described.[80] The interaction of these compounds with metal cations entails an intramolecular charge transfer. The cationic selectivity of the ligands is inferred from the changes in the electronic spectra.

The open-chain multidentate Schiff bases (XII)—derivatives of diketones, diamines, and aromatic aldehydes—as well as ligands (XIII) in which oxime residues serve as the end groups have been synthesised in order to investigate the influence of the ligand structure on the complex formation reaction.[81,82]



(XII), A = $(CH_2)_n$ ($n=2$, 3); 2,2'-bisphenylene;
R = $CH_2C(O)CH_3$, $CH_2C(O)Ph$, 2-HOC_6H_4, 3-HOC_6H_4, 2-hydroxy-1-naphthylene, 2-pyridyl, 5-(α'-picolinyl), R' = H, CH_3.



(XIII), $n = 1 \div 3$, A = CH_2OCH_2, 

X = N, CH, Cl, $COCH_3$, CNO_2;
R = C (O) CH_3, 2-$R^1C_6H_4$ (R^1 = OH, OCH_3), 4-$CH_3OC_6H_4$, 2-R^1-5-$R^2C_6H_3$ (R^1 = H, OH, CH_3, R^2 = H, OCH_3, NO_2); R^1 = H, CH_3.

The reduction of the ligands (XII) having pyridyl or picolinyl groups at the ends led to the formation of the corresponding tetraamine ligands.[83]

The formation of complexes by certain monopodands in solution has been studied.[70,75,80,84–87] Table 2 lists the logarithms of the stability constants of the complexes of ligands with alkali and alkaline earth metal cations in organic solvents. Metal thiocyanates were used for compounds (I), (II), (IX), and (XIX) as well as nigericin and 18-crown-6. The formation of complexes by the ligands (V) with sodium perchlorate was studied. Lithium, magnesium, and calcium nitrates, sodium, potassium, and rubidium thiocyanates, and barium perchlorate were used for compounds (XIV).

With increase in the strength of the electron-donating properties of the end groups of the ligand (I), (IIa, b), and (IX) with a tetra(ethylene glycol) chain, the stability of the complexes formed by them also increases, as shown by the stability constants. The diphenyl ether of tetra(ethylene glycol) (IIa) exhibits a very weak tendency towards the formation of complexes with alkali metal cations with the exception of potassium. The stability constant of the potassium complex is comparable to those for the ligands (IIb) and (IX). The author suggests that, since the π-electron interaction with the metal ion weakly stabilises the pseudoring, the size of the coordination sphere determines the most favourable conformation of the ethylene glycol chain. On replacement of one phenyl ring by the quinoline group [as in ligand (IX)], the stability constant increases, especially for the large rubidium and caesium cations. The selectivity with respect to potassium is then maintained but is less pronounced than in the case of the ligand (IIa). The introduction of the *o*-nitro-group into the phenyl substituent appreciably improves the complex-forming properties of the podand. The authors explain the preferential formation of complexes by the ligand (IIb) with large cations by the electrostatic repulsion of the *o*-nitrophenyl end groups. The compound with two quinoline end groups [compound (I)] exhibits the most effective complex-forming properties. The partial stacking interaction of the quinoline groups stabilises the pseudocyclic conformation of the complex.[88] Thus the additional electron-donating centres of the rigid end groups play an important role in the stabilisation of the complexes.

Crystalline complexes of monopodands with alkali, alkaline earth, and transition metal ions, lanthanide and actinide ions, and the ammonium cation have been obtained.[1,55,72,77] The complexes are formed as a rule with an exact stoichiometric composition even in the presence of a large excess of one of the components.

Crystalline complexes could not be obtained for analogues of compounds (I)–(III) in which the quinoline and *ortho*-methoxyphenyl end groups are linked by a hydrocarbon chain made up of 8 or 9 carbon atoms.[65,89,90] Crystalline complexes were not obtained for analogues of the ligands (II) with *meta*-methoxy-groups either.[89] Glycols with phenyl end groups [compounds (II)] form crystalline complexes only in the presence of at least five oxygen atoms in the chain.[65,75] Compounds with aromatic bridges, carrying substituents [compound (VII)] also do not afford solid complexes.[57,65]

Open-chain multidentate Schiff bases with various rigid end groups [compounds (XII)] are capable of forming crystalline complexes with transition metal ions.[81,82]

Compounds (XIII) with hydroxyphenyl or methoxyphenyl end groups as well as ligands containing diacetyl monoxime units at the ends of the oligo(ethylene glycol) chain have the (*E*)-configuration and do not form crystalline complexes. Some of them can transfer sodium or potassium permanganate to an organic medium.[82]

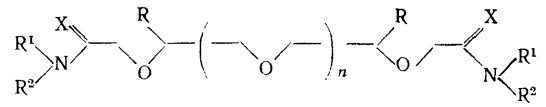
Data on the structures of the complexes of monopodands with alkali and alkaline earth metal ions have been obtained by X-ray diffraction.[1,88,91–94] Podands, which are open-chain ligands, do not have a ready made cavity in which the metal cation could be accommodated. However, during the complex-formation process they form such a cavity in one way or another. The podand molecule can twist into a ring or a helix around the cation.

Podands form crystalline complexes with neutral molecules similar to the crown-ether complexes of the "guest–host" type.[17,95–97]

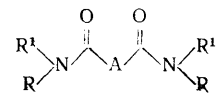
4. Membrane-active monopodands

The ability of podands to interact with metal cations is used in membrane processes. However, there is no direct relation between the effectiveness of the complex-forming agent and its membranotropic properties. Ligands which are effective complex-forming agents for alkali and alkaline earth metal cations are not always good agents for the transfer of ions through membranes. Ion transport can be achieved subject to the condition that the complex formation process is selective and dynamic. It has been shown that[98] there exists a range of optimum stability constants of complexes for the most effective transport of cations. Above and below this range, the rate of transport falls sharply. For a series of alkali and alkaline earth metal cations, ion transport is slight or is altogether absent if the logarithms of the complex formation constants in methanol are less than 3.5–4.0 units.

Open-chain ligands of the amide type with aromatic or hydrocarbon substituents and with a long chain at the nitrogen atom are selective agents transferring alkali and alkaline earth metal ions through liquid membranes [compounds (XIV) and (XV)].[15,16,86,99–105]

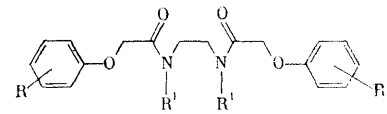


(XIV), $n = 0 \div 2$, X = O, S; $R = R^1 = R^2 = Alk$
$R^1 = (CH_2)_m CO_2Alk$ ($m = 1 \div 11$)



(XV), $A = CH_2OCH_2CH_2OCH_2$, CH_2OCH_2;
$R = CH_3$, $R^1 = C_7H_{15}$, $(CH_2)_5COOC_4H_9$;
$R = R^1 = Alk$, CH_2COOCH_3, Ph

Symmetrical ligands (XVI) containing amide and ether groups are known.[106]



(XVI), $R = o\text{-}NO_2$, $o(m)\text{-}NHCOCH_3$, $R' = H$, CH_3.

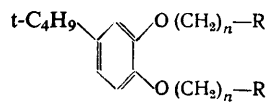
The selectivity of such ionophores with respect to cations is determined mainly by the nature and number of coordination centres and the nature of the substituents at the nitrogen atoms. An increase in the polarity of the ligand molecule leads to the preferential formation of complexes with cations having small radii. The ethylene glycol ligands (XIV) with ω-ethoxycarbonyldecyl, ω-ethoxycarbonylundecyl, or phenyl substituents are selective ligands in relation to alkaline earth metal cations[15,17,86,104] (Tables 2 and 3). The introduction of higher alkyl groups such as hexyl, octyl, decyl, undecyl, and heptadecyl at the nitrogen atom leads to the

Table 3. Potentiometric selectivity coefficients ($K^{pot}_{M_i,M_j}$) of electrodes with liquid membranes containing neutral ligands.

Structure	Material of membrane	M_j									Refs.
		H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	
					(XIV)						
$n=0$, X=O, R=H, $R^1=R^2=C_6H_{13}$	*o*-Nitrophenyl octyl ether	20	$3\cdot10^{-3}$	$5\cdot10^{-2}$	$6\cdot10^{-3}$	$1\cdot10^{-4}$	$8\cdot10^{-4}$	$3\cdot10^{-5}$	1	$3\cdot10^{-1}$	[99]
$n=0$, X=O, R=H, $R^1=(CH_2)_{10}CO_2C_2H_5$ $R^2=CH_3$	*p*-Ethylnitrobenzene	—	$3\cdot10^{-3}$	$7\cdot10^{-3}$	$9\cdot10^{-2}$	$2\cdot10^{-1}$	$6\cdot10^{-2}$	$3\cdot10^{-5}$	1	$8\cdot10^{-2}$	[15]
$n=0$, X=O, $R=R^2=CH_3$ $R^1=(CH_2)_{11}CO_2C_2H_5$	*o*-Nitrophenyl octyl ether	—	$2\cdot10^{-2}$	$1\cdot10^{-2}$	$6\cdot10^{-3}$	$1\cdot10^{-2}$	$9\cdot10^{-3}$	$1\cdot10^{-4}$	1	$1\cdot10^{-3}$	[86]
$n=0$, X=O, R=H $R^1=R^2=CH_2Ph$	Ditto	1	—	1	$2\cdot10^{-1}$	—	—	$3\cdot10^{-4}$	$6\cdot10^{-3}$	$4\cdot10^{-2}$	[17]
$n=0$, X=O, R=H $R^1=R^2=Ph$	»	—	$6\cdot10^{-4}$	$7\cdot10^{-1}$	$3\cdot10^{-1}$	$5\cdot10^{-2}$	$1\cdot10^{-2}$	$4\cdot10^{-5}$	$7\cdot10^{-3}$	1	[86]
$n=1$, X=O, R=H $R^1=R^2=Ph$	»	$9\cdot10^{-2}$	$5\cdot10^{-3}$	$2\cdot10^{-2}$	$4\cdot10^{-2}$	$2\cdot10^{-2}$	$6\cdot10^{-3}$	$4\cdot10^{-5}$	$8\cdot10^{-4}$	1	[104]
$n=0$, X=O, R=H $R^1=C_3H_7$, $R^2=t\text{-}C_4H_9$	»	10	—	$2\cdot10^{-2}$	$2\cdot10^{-2}$	—	—	$3\cdot10^{-4}$	1	$8\cdot10^{-3}$	[17]
					(XVII)						
$n=2$, R=S(O)CH_2Ph	*o*-Nitrophenyl octyl ether	2.6	$3.6\cdot10^{-2}$	$7.4\cdot10^{-3}$	$1.6\cdot10^{-2}$	—	—	$6.8\cdot10^{-3}$	1	—	[102]
$n=3$, R=S(O)Ph	Ditto	$5.4\cdot10^{-2}$	$9.3\cdot10^{-3}$	$1\cdot10^{-3}$	—	—	—	$8.5\cdot10^{-3}$	1	—	[102]
					(XX)						
R=cyclo-C_6H_{11}, R^1=Ph	Bis(1-butylpentyl) adipate	—	4	1	$5\cdot10^{-2}$	$2\cdot10^{-2}$	$8\cdot10^{-3}$	$2\cdot10^{-4}$	$5\cdot10^{-3}$	$5\cdot10^{-3}$	[101]
					(XXVIII)						
$m=1$, $R=CH_3$, $R^1=C_7H_{15}$, $R^2=C_2H_5$	*o*-Nitrophenyl octyl ether	$2\cdot10^{-1}$	2.8	1	$4.4\cdot10^{-3}$	$3.6\cdot10^{-3}$	$2.9\cdot10^{-3}$	$1.7\cdot10^{-3}$	$2.9\cdot10^{-1}$	$4.4\cdot10^{-2}$	[15]
$m=2$, $R=R^2=CH_3$, $R^1=C_7H_{15}$	Dibenzyl ether	—	1	$5\cdot10^{-2}$	$8\cdot10^{-3}$	$5\cdot10^{-3}$	$6\cdot10^{-3}$	$4\cdot10^{-4}$	$8\cdot10^{-4}$	$5\cdot10^{-4}$	[104]
$m=2$, $R=CH_2CH_2OC_2H_5$, $R^1=C_7H_{15}$, $R^2=CH_3$	Soyalipid	—	1	$7\cdot10^{-2}$	$1.6\cdot10^{-2}$	$0.5\cdot10^{-3}$	$8.3\cdot10^{-3}$	—	—	—	[110]
Nonyl phenyl ether of poly(ethylene glycol).$[Ba(BPh_4)_2]_7$	*p*-Ethylnitrobenzene	$2\cdot10^{-4}$	$2\cdot10^{-4}$	$2\cdot10^{-4}$	$8\cdot10^{-3}$	—	—	$<1\cdot10^{-4}$	$<1\cdot10^{-4}$	1	[15]
Dibenzo-18-crown-6-ether	»	—	—	$4.1\cdot10^{-2}$	1	$3.5\cdot10^{-1}$	$2.7\cdot10^{-1}$	—	—	—	[5]
Valinomycin	Diphenyl ether	$5\cdot10^{-5}$	$2\cdot10^{-4}$	$2.5\cdot10^{-4}$	1	1.9	$4\cdot10^{-1}$	$<2\cdot10^{-4}$	$<2\cdot10^{-4}$	—	[5]

preferential interaction with the calcium cation.[99,106] With increase in lipophilicity, the ionophoric properties of these compounds vanish owing to the kinetically limited exchange reaction between the aqueous phase and the membrane. The dioxadithioamide (XIV) with butyl substituents at the nitrogen atom is a highly selective ionophore for the cadmium ion.[15] The potentiometric selectivity series for this ligand is Cd (1) > Li (1×10^{-3}) > K (8×10^{-4}) > Cs (3×10^{-4}) > Na (1×10^{-4}) = Rb (1×10^{-4}) > Ca (5×10^{-5}) = Ba (5×10^{-5}) > Mg (1.5×10^{-5}). It follows from the data presented that, with the aid of an ion-selective electrode containing a given ligand, it is possible to determine the content of cadmium ions in a mixture with other cations whose concentration is higher by 3–5 orders of magnitude. The *NNN*^{1}*N*^{1}-tetracyclohexyl-substituted diamide (XV) with A = CH_2OCH_2 exhibits selective properties in relation to the calcium ion in the presence of magnesium ions with a separation factor of 10^4.[100]

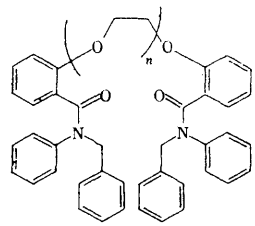
The acyclic polyethers (XVII) with sulphenyl groups are selective in relation to the calcium cation[102] (Table 3).



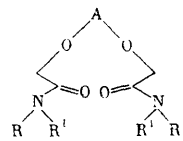
(XVII), R= S(O)C_6H_5, S(O)$CH_2C_6H_5$, S(O)C_8H_{17}-*n*

Ligands with rigid units between the amide end groups [compounds (XVIII)–(XXI)], exhibiting selectivity with respect to sodium in the joint presence of sodium and potassium ions

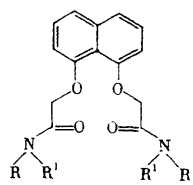
(separation factor of 20), have been obtained.[101,103,107]



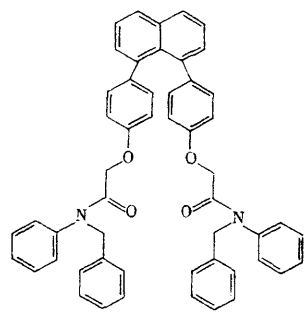
(XVIII)



(XIX)



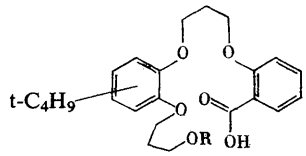
(XX)

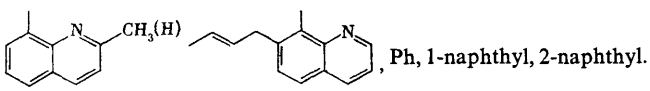


(XXI)

(XVIII), $n = 0$, 1; (XIX), A = 1,2-phenylene, 2,2′-bisphenylene, or 2,3-naphthylene; R = cyclo-C_6H_{11} or Ph, $R^1 = (CH_2)_{11}CO_2C_2H_5$, cyclo-$C_6H_{11}$, or $CH_2C_6H_5$; (XX), $R = R^1$ = cyclo-C_6H_{11}; $R^1 = CH_2C_6H_5$.

Few acyclic ligands selective with respect to lithium ions relative to sodium ions are known.[15,108,109] The creation of lipophilic ionophores for lithium is difficult because the lithium ion has the smallest radius among alkali metals and exhibits a very high capacity for hydration. These ligands are mainly acid in character.

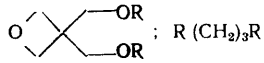




R = , Ph, 1-naphthyl, 2-naphthyl.

Ethylene and tri- and tetra-methylene derivatives have been obtained.[87,110] Ligands with two trimethylene units exhibit the highest selectivity with respect to lithium.

A series of ionophores with a high selectivity with respect to lithium were synthesised recently by the reaction of 3,3-bis(chloromethyl)oxetan or other dihalides with 8-quinolinols.[111]



; R $(CH_2)_3$R

R = 8-quinolinyl.

The selectivity coefficient with respect to lithium relative to sodium is 110 for oxetan with 8-hydroxyquinoline groups. This is the best of the known lithium transferring agents.

The parameters of the membrane electrodes in which neutral complex-forming agents are used are listed in Table 3. The selectivity of the complex formation reaction is influenced by the medium of the membrane. With increase in the polarity of the medium, the stability of the complexes falls.[87]

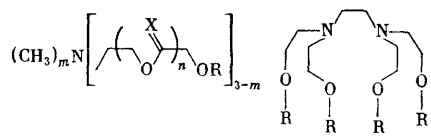
It has been shown by ^{13}C NMR spectroscopy[107,112] that in solution amide ligands of type (XIV) form complexes with ligand : metal = 1 : 1 and 2 : 1 compositions. The amide and ether oxygen atoms and in 1 : 1 complexes the carbonyl groups (as a rule) participate in coordination to the cation. Crystalline complexes with alkaline earth and transition metal salts are stabilised by water molecules.[103]

Monopodands with rigid end groups occupy an intermediate position between oligo(ethylene glycols), on the one hand, and glymes and crown-ethers, on the other, as regards their complex-forming properties. The simplest method of synthesis of monopodands, which does not require a high dilution or the use of a matrix method, and high yields of products are all advantages of the open-chain ligands over their cyclic analogues.

III. Oligo(poly)podands

1. Acyclic analogues of cryptands

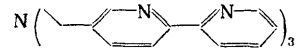
The high complex-forming capacity of bicyclic nitrogen-containing polyethers — cryptands[113] — stimulated the synthesis of their acyclic analogues,[66,114–119] which are open-chain ligands with several polyether chains diverging from the central nitrogen atom. Ligands of this type are combined under the general name oligo(poly)-podands.[2] The oligo(ethylene glycol) chains of these compounds have different end groups. Ligands based on ethanolamines with hydroxy-end groups are known. The alkyl groups in polypodands can be replaced by rigid phenyl, quinolinyl, and tropolone groups [compounds (XXII)–(XXV)].



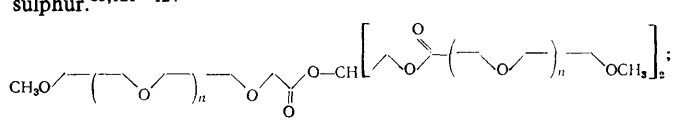
(XXII),(XXIII) (XXIV) (XXV)

(XXII), $m = 1$, $n = 0$, $X = H_2$; (XXIII), $m = 0$, $n = 0-3$, $X = H_2$, O; (XXII)–(XXIV), R = H, Alk, Ph, 2-$R^1C_6H_4$ ($R^1 = CH_3$, OCH_3, NO_2); 2,6-$(CH_3O)_2C_6H_3$, 8-quinolinyl, 2-tropolonyl; (XXV), $n = 0$, 2, R = Alk, CH_2OCH_3, $CH_2(OCH_2CH_2)_2OC_4H_9$, R^1 = Alk.

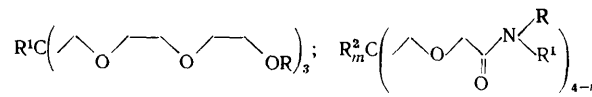
Tri- and tetra-podands containing 4-aminomethylene-2,2′-bipyridyl groups as complex-forming fragments have been synthesised.[120]



The central nitrogen atom in compounds of type (XXII)–(XXV) can be replaced by carbon [compounds (XXVI)–(XXVIII)] or sulphur.[85,121–124]

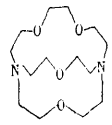
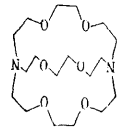


(XXVI), $n = 2$, 3



(XXVII), R = H, Alk, R^1 = Alk (XXVIII), $m = 1$, 2, R = Alk, Ph, R^1 = Alk, R^2 = Alk

Table 4. The logarithms of the stability constants of complexes of polypodands with alkali and alkaline earth metal chlorides.

No. of compound	R	n	lg K_{st}				Solvent	Refs.
			Li^+/Na^+	K^+/Cs^+	Mg^{2+}/Ca^{2+}	Sr^{2+}/Ba^{2+}		
(XXIIa)	8-Quinolinyl	—	<2/<2	<2/<2	<2/<2	<2/<2	$CH_3OH:H_2O$ (88:12)	[115]
(XXIIb)	2-Tropolonyl	—	<2/2.0	<2/<2	<2/2.1	2.5/2.6	»	[115]
(XXIII)	8-Quinolinyl	0	<2/2.7	2.0/<2	2.06/2.14	2.7/3.2	»	[115]
(XXIII)	8-Quinolinyl	0	2.18/3.69	2.58/1.57	—	—	CH_3OH	[75]
(XXIII)	2-Tropolonyl	0	<2/<2	<2/<2	<2/<2	3.3/3.6	$CH_3OH:H_2O$ (88:12)	[115]
(XXIV)	8-Quinolinyl	0	<2/2.1	2.1/<2	<2/<2	2.1/2.8	»	[115]
(XXIV)	2-Tropolonyl	0	—/2.5	—	—/2.7	3.0/3.1	»	[115]
(I) *	8-Quinolinyl	3	2.37/3.22	3.51/2.6	4.99/—	—	CH_3OH	[65, 75]
—		—	7.58/6.08	2.24/<2	4.0/4.34	2.9/<2	$CH_3OH:H_2O$ (95:5)	[125]
—		—	1.8/7.21	9.75/3.54	<2/7.6	11.5/12	»	[125]

* Metal thiocyanates were used as the salts.

The stability constants of the complexes formed by open-chain cryptands with alkali metal, alkaline earth metal, and lanthanide cations have been determined by spectrophotometric[65,75] and potentiometric[115,125,126] methods. The most stable complexes are formed by these ligands with cations having large radii—sodium, potassium, strontium, and barium. The logarithm of the stability constant of the barium complex of the tripodand (XXIII, n = 1) with 8-hydroxyquinoline end groups is 4 units.[127] The end groups play an appreciable role in complex formation. Thus ligands with tropolone groups form more stable complexes than their analogues with quinolinyl groups (Table 4). For ligands with the same number of units in the oligo(ethylene glycol) chain, the stability of the complexes increases with enhancement of the electron-donating capacity of the end group in the sequence C_6H_5 < 2-$NO_2C_6H_4$ ⩽ CH_3 < 2-$CH_3OC_6H_4$ ⩽ 8-quinolinyl.[127] It is of interest that the tetrapodands (XXIV) form more stable complexes than the analogous dipodands (XXII) but less stable than the tripodands (XXIII). This is attributed to the steric hindrance which may be generated by the four bulky end groups.

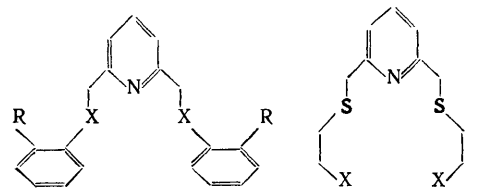
Comparison of the complex-forming properties (Table 4) of the tripodand (XXIII) and the tetraethylene glycol monopodand with quinolinyl end groups [compound (I)], having the same number of electron-donating atoms, shows that in the series of alkali metals this ligand is only slightly superior to the monopodand (I) only in the case of the sodium cation. As regards other di-, tri- and tetrapodands, they all form less stable complexes with alkali metal cations than the monopodand (I). This permits the conclusion that the simpler monopodands are also more effective for alkali metal cations. It is noteworthy that bicyclic nitrogen-containing ligands (cryptands) form very stable complexes with alkali and alkaline earth metal cations[125] but they are difficult to obtain.

In contrast to nitrogen-containing podands, the complex-forming properties of the carbon ligands are much weaker.[85,87] The logarithms of the stability constants of the complexes of the ligands (XXVI, n = 2) and (XXVII) with sodium perchlorate in pyridine are 2.0 and 1.3 respectively.

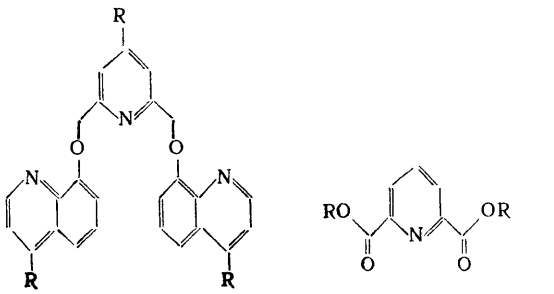
Numerous crystalline complexes with alkali, alkaline earth, transition, and other metal salts have been obtained for the open-chain cryptand analogues.[51,127–129] The tripodand (XXIII, n = 1), having methylquinolinyl groups, forms crystalline complexes with neutral molecules such as those of urea, 4-nitrophenylhydrazine, and water.[17,130]

Compounds whose characteristic structural elements are central pyridine and pyridine oxide units constitute a separate group of acyclic multidentate ligands—dipodands. A general method of synthesis of compounds with one pyridine unit [compounds (XXX)–(XXXII)] consists in the interaction of 2,6-di(halogenomethyl)piperidine with phenols or thiols in the presence of a base.[57,84,114,131] Their oxidation with hydrogen peroxide can afford the corresponding *N*-oxides.[132]

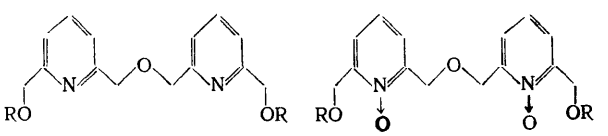
Pyridine ligands with ester groups [compound (XXIII)] have been synthesised.[72] Compounds containing two pyridine or pyridine oxide units [compounds (XXXIV) and (XXXV)] are known.[132–134]



(XXX), X=O, S; R=H, Hal, NO_2, OAlk, CO_2Alk (XXXI), X=H, OH, NH_2



(XXXII), R=H, Cl CH_3O, $N(CH_3)_2$ (XXXIII), R=Alk, $CH_3OCH_2CH_2$, $ClCH_2CH_2$



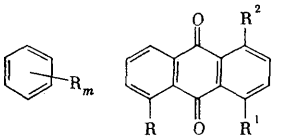
(XXXIV) (XXXV)

(XXXIV), (XXXV), R=H, OH, OAc, 8-quinolinyl, 8-(2-methylquinolinyl), 2-$H_3COC_6H_4$, 2,6-$(CH_3O)_2C_6H_3$.

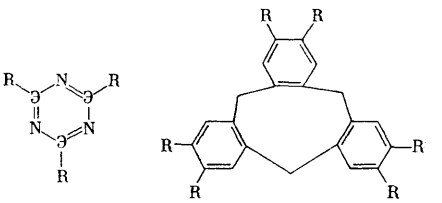
Representatives of compounds of this type form very readily crystalline complexes with alkali, alkaline earth, and heavy metal ions.[15,57,72,84] Ligands with pyridine oxide units exhibit a reduced complex-forming capacity in relation to alkali metal cations.[132] The introduction of pyridine units into the polyether chain imparts rigidity to the ligands, which greatly improves their selectivity in relation to alkali metal cations.[75,84] It is of interest that classical ligands for transition metal ions, such as bipyridyl, terpyridyl, and phenanthroline, form stable complexes with alkali and alkaline earth metal salts.[135,136] Ligands of the ester type (XXXIII) do not form complexes with heavy metals.[72] Certain compounds with pyridine and pyridine oxide units afford crystalline complexes with urea, thiourea, malodinitrile, and water.[132,137]

2. "Octopus-like" polypodands

The number of oligoether chains in polypodands can be increased by combining them with some kind of binding centre. Ligands with six and more multidentate chains whose electron-donating centres consist of oxygen, sulphur, selenium, and nitrogen atoms have been obtained in this way. The benzene ring [compound (XXXVI)] has been used as the binding fragment.[66,138–140] These ligands have been synthesised by treating hexa(bromomethyl)benzene in the presence of a base with the corresponding phenol, thiol, or selenol.



(XXXVI) (XXXVII)

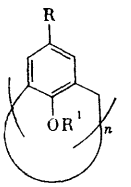


(XXXVIII) (XXXIX)

(XXXVI), $R=CH_2X(CH_2CH_2O)_nAlk(Ph)$, X=O, S, Se, $n=0-3$, $m=2-6$;
(XXXVII), $R=R^1=O(CH_2CH_2O)_3CH_3$, $R^2=H$, $R=R^2=O(CH_2CH_2O)_3CH_3$, $R^1=H$;
(XXXVIII), E=C, P(V), $R=N[(CH_2CH_2O)_4Alk]_2$, $(OCH_2CH_2)_nOAlk$;
(XXXIX), $R=(OCH_2CH_2)_3Alk$.

Treatment of 1,5- or 1,8-dichloroanthraquinone with the monomethyl ether of triethylene glycol in the presence of sodium hydride led to the synthesis of podands[141] with the anthraquinone unit [compounds (XXXVII)].

Polyether chains may be present in triazine, or cyclophosphazene [compound (XXXVIII)] and cycloveratrylene [compound (XXXIX)] systems.[123,142] Oligoethylene glycol units can be combined in a matrix made up of cyclic oligomers obtained under the conditions of base catalysis.[143,144] Multidentate chains are introduced into these compounds instead of hydroxy-groups via the tosylates of the corresponding cellosolves.[145–148] Such macrocyclic compounds have been called spherands or calixarenes (XL).



(XL)

(XL), $n=4, 6, 8$; R = H, Alk; R^1 = Alk, $(CH_2CH_2O)_nAlk$.

Since the complex-forming capacity of these ligands is mainly determined by the structure of the side chains carrying electron-donating centres, they can be regarded as a variety of podands.

The complex-forming capacity of the ligands (XXXVI)–(XXXIX) decreases with decrease in the number of their binding sites. Compounds (XXXVI) with six short chains, terminating in thiophenyl or thiocycloalkyl groups, do not interact with metal ions but do form inclusion compounds with neutral organic molecules.[140,149] "Octopus-like" polypodands whose chains terminate in rigid electron-donating groups form crystalline complexes with derivatives of urea, pyridine, amides, nitriles, diglyme, and crown-ethers.[150] Trisubstituted benzenes do not give rise to inclusion compounds.[139] Crystalline complexes of calcium and barium thiocyanates with a trisubstituted benzene having amide groups have been isolated.[66]

Polypodands based on a cyclic oligomeric matrix — the spherands (XL) — exhibit complex-forming properties in relation to alkali metal cations. The formation of complexes by these compounds with lithium and sodium perchlorates and picrates has been observed by NMR spectroscopy.[151,152] The sodium complex of a calix[4]arene ($R^1 = CH_3$), in which the sodium ion interacts with all four oxygen atoms, has been isolated.[153] The high selectivity of spherands based on anisole with $n = 6$ in relation to lithium and sodium ions in the series of alkali metals has been demonstrated.[154] There exist data indicating a high extracting capacity of spherands with $n = 6$ and 2-methoxy-groups in aromatic rings in relation to guanidine.[147] However, the complex-forming capacity of these compounds is appreciably inferior to that of its analogues in which R^1 consists of ester or amide groups.[148,153,155–157]

Thus the increase in the number of binding sites in the ligands achieved by including additional oligoethylene glycol chains in the podand molecules constitutes yet another way of enhancing their complex-forming properties. The replacement of electron-donating ether oxygen atoms by other heteroatoms or groups with an enhanced nucleophilicity also makes it possible to improve the complex-forming capacity of podands. However, the increase in the complexity of the structure of such ligands makes them less available.

IV. Applications of neutral acyclic complex-forming agents

At the present time, the number of studies devoted to the practical use of podands is small but these compounds have considerable potential possibilities for applications in chemistry and technology. The most thoroughly investigated field in which podands are used is phase transfer catalysis, which constitutes a promising method for effecting chemical reactions.[9–12] Oligo- and poly-ethylene glycols accelerate the nucleophilic substitution reactions at a carbon atom between anions and water-insoluble neutral organic compounds in two-phase systems. Systems incorporating different potassium salts, carboxylic and sulphonic acid chlorides, and alkyl halides have been investigated[29,32,76,158–165] (Table 5). The effectiveness of oligo- and poly-ethylene glycols and their ethers increases with increase in concentration and in the molecular weight of the ligand. Polyethylene glycols with a molecular weight in excess of 400 can be used as phase transfer catalysts (Table 5) whose activity depends on the specific system. The increase in the rates of nucleophilic reactions in the presence of polyethylene glycols has been explained by the cooperative solvation of alkali metal cations by oxygen atoms leading to the activation of the anions.[166]

The use of monopodands based on catechol with quinolinyl end groups as phase transfer catalysts increases by a factor greater than 2–3 the yield of the product (Table 5). The application of "octopus-like" ligands (XXXVI) in reactions of alkyl halides with potassium cyanide increases the yield by a factor of 10.[167] Derivatives of 1,3,5-triazine (XXXVIII) proved to be effective catalysts in any anionic reactions.[123,142] The activity of these ligands increases with increase in the number of binding sites of the oligoethylene glycol chains and also in the length of the alkyl groups at their ends. The catalytic properties of triazine ligands resemble those of tetraalkylphosphonium salts. Comparison of the catalytic activities of crown-ethers, cryptands, glymes, and poly(ethylene glycols) showed that the cryptand 222 is the most effective. Decaglyme is not inferior to 18-crown-6-ether and tetrabutylammonium perchlorate, while the effectiveness of poly(ethylene glycol) (Carbowax-20M) is similar to that of dibenzo-18-crown-6 [163] (Table 6).

Table 5. Yields of products in certain nucleophilic substitution reactions using podands as phase transfer catalysts.

Catalyst	Structure	Reaction conditions	Yield, %
$C_4H_9Br + KI \rightarrow C_4H_9I + KBr$ (Ref.159)			
—	—	1.5 h, refluxing, water	13
$HO(CH_2CH_2O)_3OH$	—	ditto	27
PEG-1000	—	»	50
PEG-2000	—	»	96
PEG-6000	—	»	96
Dibenzo-18-crown-6	—	»	45
$C_6H_5CH_2Br + CH_3COOK \rightarrow C_6H_5CH_2OCOCH_3 + KBr$ (Ref.164)			
$H_3CO(CH_2CH_2O)_8CH_3$	—	CH_3CN, 1 h, 20 °C	96
18-Crown-6	—	CH_3CN, 2 h, 25 °C	100
$C_6H_5CH_2Cl + CH_3COOK \rightarrow C_6H_5CH_2OCOCH_3 + KCl$ [76]			
—	—	CH_3CN, 2 h, refluxing	29
(IX)	$n=2$, $R=CH_3C(O)$	ditto	98
	$n=3$, $R=CH_3C(O)$,	»	88
	2-CH_3O-4-$CH_3C(O)C_6H_3$	»	68
$n\text{-}C_8H_{17}Br + KI \rightarrow n\text{-}C_8H_{17}I + KBr$ (Refs. 123, 142)			
(XXVII)	$R=CH_2CH_2OH$; $R^1=CH_2OC_{10}H_{21}$	H_2O, 72 h, 60 °C	87
»	$R=n\text{-}C_8H_{17}OCH_2CH_2$ $R^1=CH_2OC_{10}H_{21}$	H_2O, 10 h, 80 °C	<1
(XXXVIII), E=C	$[n\text{-}C_4H_9(OCH_2CH_2)_4]_2N$	H_2O, 72 h, 60 °C	82
»	$[n\text{-}C_8H_{17}(OCH_2CH_2)_4]_2N$	H_2O, 3 h, 60 °C	85
(XXXVIII), E=P(V)	$n\text{-}C_8H_{17}(OCH_2CH_2)_3O$	»	42
»	$n\text{-}C_8H_{17}(OCH_2CH_2)_2O$	H_2O, 8 h, 80 °C	88
$(C_4H_9)_3C_{10}H_{21}PBr$	—	H_2O, 3 h, 60 °C	72

The catalytic activity of glymes with $n = 1–4$, 10, 21 in the aminolysis of esters[168] is higher than that of crown ethers with the same number of oxygen atoms (Table 6).

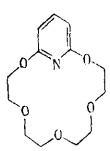
Poly(ethylene glycols) and their ethers can be used as phase transfer catalysts in *N*- and *S*-alkylation reactions.[169–172]

The tripodands (XXIII, $n = 1$, $m = 0$, $X = H_2$) constitute a new class of phase transfer catalyst in a solid–liquid system.[173]

An important field where podands can be used is extraction. Thus poly(ethylene glycols) containing more than 23 units exhibit strong extracting properties in relation to potassium, which are comparable to those of 18-crown-6[174,175] (Table 7). Poly(ethylene glycols) with molecular weights ranging from 400 to 4000 are more effective extractants for lead and strontium than dibenzo-18-crown-6

and dibenzo-24-crown-8 but are inferior to 18-crown-6.[176,177] Oligo(ethylene glycols) with nitrile end groups can be used to extract alkali metals from boracic water in the presence of a large excess of alkaline earth elements.[178] The sulphur-containing podand 1,12-di-2-thienyl-2,5,8,11-tetrathiadodecane extracts silver ions quantitatively from dilute aqueous solutions.[179] An asymmetric monopodand, at the ends of oligo(ethylene glycol) chain (n = 11) of which there are substituted aryl groups, extracts alkali and alkaline earth metal cations with formation of 1 : 1 complexes.[180]

Table 6. Catalytic activities of different catalysts.

Catalyst	Relative rate of reaction
$KSCN + n\text{-}NO_2C_6H_4CH_2Br \xrightarrow{CHCl_3-H_2O} n\text{-}NO_2C_6H_4CH_2SCN +$ + KBr (Ref.163)	
18-Crown-6	1.44
Benzo-18-crown-6	1.23
Dibenzo-18-crown-6	1.00
Dicyclohexyl-18-crown-6	1.65
Cryptand 222	5.10
Decaglyme	1.41
$(C_4H_9)_4NClO_4$	1.29
Carbowax 20 M	0.88
$CH_3COOC_6H_4NO_2\text{-}p + NH_2C_4H_9 \xrightarrow{PhCl} p\text{-}HOC_6H_4NO_2 +$ + $CH_3CONHC_4H_9$ (Ref.168)	
$CH_3(OCH_2CH_2)_nOCH_3$	
n=1	1
n=2	4.9
n=3	11
n=4	14
n=10	37
n=22.3	76
6-Crown-2	0.52
9-Crown-3	2.8
12-Crown-4	5.2
15-Crown-5	8.8
	0.29

Another possible application of podands is association with their ability to solubilise salts in solvents of low polarity. This makes it possible to carry out a whole series of reactions under homogeneous conditions in non-polar media. The nitrogen-containing tripodands (XXIII) transfer potassium permanganate and alkali metal picrates to the organic phase much more readily than dibenzo-18-crown-6.[118] In the presence of poly(ethylene glycols), it is possible to dissolve metallic potassium in benzene[181] and potassium permanganate in organic solvents[182] and alkenes can be oxidised by potassium permanganate.[160,161]

A series of applications of podands are associated with their membrane activity. Some of them can be used in cation-sensitive membrane electrodes specific to alkali and alkaline earth metal ions (Table 3). Thus the complex $Ba(BPh_4)_2$ with nonyl phenyl ether of poly(ethylene glycol) (n = 30) is used in a barium-sensitive electrode.[15] The neutral acyclic diamide [XIV, n = 0, X = O, R = CH_3, R^1 = $(CH_2)_{10}COOC_2H_5$] is used in a calcium-selective electrode.[5] Many polydentate ligands, such as the oxa-analogues of diamides of sebacic and azelaic acids (XIV), are known. They are selective transferring agents for lithium and sodium ions in the presence of protons and calcium, strontium, and barium ions.[15,17,86,99–101,104,108,183] A study of the membrane activity of tetraethylene glycol with quinoline end groups showed that this ligand transfers ammonium cations selectively through a liquid membrane in the presence of alkali metal ions.[184] The tripodand (XXIII, n = 1, X = H_2) exhibited effective and specific transport properties for silver ions.[119] Podands of the type of spherands (XL) can also be used in membranes.[144]

Table 7. The extracting capacities of certain ligands in relation to alkali metal salts in the H_2O-CH_2Cl system.[174,175]

Ligand	c_L, M	% in CH_2Cl_2		
		0.85×10^{-4} M Na picrate	0.95×10^{-4} M K picrate	1.0 M KSCN
	—	0.7	0.7	—
15-Crown-5	0.00058	1.5	1.7	—
18-Crown-6	0.00056	2.4	17.3	—
PEG-400	0.02	—	—	6
PEG-600	0.02	—	—	14
PEG-1000, n=23	0.00047	2.0	8.2	—
Ditto	0.00181	3.9	14.5	—
"	0.02	—	—	27
PEG-4000	0.02	—	—	100
PEG-6800	0.00027	3.6	19.2	—
"	0.00036	4.7	20.8	—

The great variety of structures of the neutral acyclic polydentate ligands makes it possible to vary their selectivity with respect to cations within wide limits. The ability of podands to form complexes with neutral organic molecules can be of pharmacological interest, particularly in the case of urea. Furthermore, the availability of these compounds makes them promising complex-forming agents which can find applications in various branches of chemistry and the national economy.

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During the preparation of the manuscript for the press, new studies on the synthesis of podands, on their complex-forming properties, and on their applications in organic synthesis were published. Thus these questions are discussed in a book.[185] New Schiff bases capable of combining in complexes transition and alkali or alkaline earth metal ions simultaneously have been synthesised.[186–188] Podands with imidazole units have been obtained and their transport properties in relation to alkali metals and ammonium cations have been investigated.[189–191] The synthesis

of chiral podands derived from carbohydrates[192–194] and from the 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene fragment[195] are being developed. A chiral ligand coordinating the lithium cation has been put forward.[196] New tripodands of type (XXVII) are selective complex-forming agents in relation to cations with a small radius.[197] Monopodands with different end groups have been obtained by opening epoxide rings in the diglycidyl ethers of poly(ethylene glycols).[198] The synthesis of new sulphonamide podands,[199] compounds based on 1,4-benzoquinone,[200] cyclohexane,[201] and a phosphazene matrix,[202] and open-chain analogues of benzo-crown-ethers[203] have been described. A report has been published on the synthesis of a new class of branched polyethers—the so-called dendrimers and arboreols.[204] Dendrimers have a spherical steric oligomeric structure. Some of them (arboreols) contain a large number of terminal OH groups.

The study of the formation of complexes by oligo- and poly-(ethylene glycols) and their ethers with alkali metal and ammonium ions[205,206] and of tripodands having a central carbon atom with the Fe^{3+} and Ga^{3+} cations by various physicochemical methods is being continued.[207] The structures of complexes of tetraglyme with the oxonium cation,[208] of penta- and hexa-glymes with calcium, strontium, and barium thiocyanates,[209,210] and of triethylene glycol with lanthanide chlorides[211] have been established. The complex-forming properties of their sulphur-containing analogues are being investigated.[212,213] The interaction of amino-derivatives of oligo-(ethylene glycol) with alkaline earth and transition metal ions is being studied vigorously.[214–219] New data have been obtained on the behaviour in solution of polyamines with various end groups in the presence of transition and other metal cations.[220–223] Their complexes with the lanthanides[224] and rhenium(V)[225] have been synthesised and characterised.

The properties of podands of different types as phase transfer catalysts are being investigated. In the presence of poly(ethylene glycols) and their derivatives, nucleophilic substitution reactions,[226–228] oxidation reactions of cyclic ketones,[229] and the dissolution of metals[230] are accelerated and oxidation-reduction processes are promoted.[231] There are new examples of the use of ligands of type (XXXVIII)[232] and of calixarenes (XL) with oligoethylene chains in the formation reactions of ethers.[233]

The extracting properties of hydrophobic dialkyl ethers of oligo-(ethylene glycols)[234] and of their analogues with electron-donating S and N atoms[235–237] in relation to alkali and alkaline earth metal cations are being investigated in relation to the similar properties of macrocyclic ligands.

Podands which could be used as electrode-active components of membranes of ion-selective electrodes are being sought.[238–239]

A method of synthesis of solid complexes of organomagnesium compounds with tris(dioxa-3,6-heptyl)amine has been described.[240] The first photophysical study of complexes of podands, coronands, and cryptands in photoelectron transfer reactions has been noted.[241]

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