SYNTHESIS AND PROPERTIES OF PODANDS WITH 4-ANTIPYRYLIMINOMETHINE GROUPS

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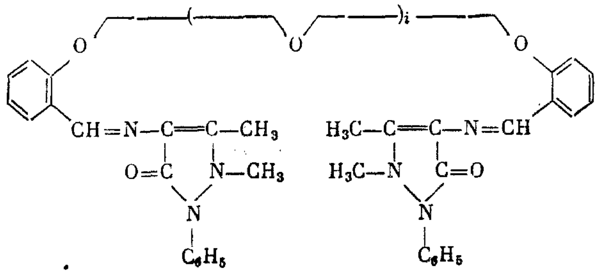
Novel podands with 4-antipyryliminomethine groups on benzenes and various numbers of ethers are prepared. According to UV spectroscopy, these compounds form complexes with alkali, alkaline earth, and transition metals. Extraction of metal picrates demonstrated that the podands selectively form extractable complexes with these salts. A lead-selective electrode with an electrode function 22-24 mV/pPb is based on 1,8-bis[2-(4-antipyryliminomethine)phenoxy]-3,6-dioxaoctane. This enables $1\cdot10^{-6}-1\cdot10^{-2}$ M Pb to be determined in the pH range 3.5-5.5. The electrode is highly selective for Pb in the presence of alkali and alkaline earth metals.

Macrocyclic compounds and their open-chain analogs (podands) are selectively ligands that form complexes with various metal cations. Their practical useful properties, in particular, in extraction and in membranes, are interesting [1-3].

In the present work, the syntheses of podands (PD) with 4-antipyryliminomethine groups on benzenes with various numbers of ethers in a polyoxyethylene chain are reported. Variation of the number of ethers changes the selectivity on complexation. Novel PD are prepared by reaction of aldehydes and amines. The compounds 1,5-bis(oxybenzaldehyde)-3-oxapentane, 1,8-bis(oxybenzaldehyde)-3,6-dioxaoctane, and 1,11-bis(oxybenzaldehyde)-3,6,9-trioxaundecane were prepared from di-, tri-, and tetraethylene glycol according to [2]. Reaction of these with 4-aminoantipyrine gave compounds with the formulas



$i = 1$(a), 2(b), 3(c).

Podands (Ia) and (Ib) are bright yellow crystalline compounds which precipitate from the reaction mixture on cooling. Podand (Ic) is isolated upon removal of solvent as a dark brown oil which solidifies after prolonged drying in vacuum. The PD prepared are very soluble in alcohols, $CHCl_3$, acetone, ethylacetate, toluene, and other solvents. They are insoluble in water and ether.

The composition and structure of the synthesized compounds were verified by elemental analysis, assignment of characteristic IR absorption bands, and study of the electronic absorption spectra (Table 1).

The presence of a C=N bond (Ia-c) was confirmed by two absorption bands in the IR spectra at 1643-1648 and 1650-1652 cm^{-1}. The $N{-}CH_3$ bond appears at 1450 and 1460 cm^{-1}. The C–H bond in CH_3 gives weak bands at 1421-1425 and 1410-1412 cm^{-1}. Bands characteristic of C(O)N

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TABLE 1. Characteristics of Podands with 4-Antipyryliminomethine Groups

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			UV spectra λ^i_{max}, nm (log ε_i)			
		C	H	N		C	H	N	i=1	i=2	i=3	i=4
(Ia)	185–186	70,19	6,19	12,21	$C_{40}H_{40}N_6O_5$	70,16	5,89	12,27	255 (5,87)	335 (5,84)	344 (5,86)	–
(Ib)	157–158	69,15	6,15	11,53	$C_{42}H_{44}N_6O_6$	69,21	6,08	11,53	299 (6,23)	333 (6,31)	342 (6,33)	
(Ic)	53–54	68,53	6,40	10,72	$C_{44}H_{48}N_6O_7$	68,38	6,26	10,87	297 (5,66)	333 (5,74)	344 (5,77)	252 (5,83)

TABLE 2. Changes in Electronic Spectra of Ligands in the Presence of Metal Salts in $CHCl_3$

Compound	Metal salt	λ^i_{max}, nm (log ε_i)			
		i=4	i=3	i=2	i=1
(Ia)		344(5,86)	335(5,84)	255(5,87)	
	Li	–	324(5,50)	297(5,46)	
	Co	343(5,69)	333(5,68)	256(5,70)	
	Cu	–	326(5,50)	255(5,71)	
	Zn	–	322(5,38)	299(5,34)	
	Hg	–	326(5,47)	256(5,79)	
	Pb	325(5,49)	295(5,61)	254(5,95)	
(Ib)		342(6,33)	333(6,31)	299(6,23)	
	Li	–	327(6,02)	254(6,33)	
	K	–	337(5,99)	255(6,20)	
	Ca	–	–	254(6,31)	
	Sr	–	337(6,26)	252(6,50)	
	Ga	–	326(6,02)	254(6,37)	
	Mn	–	329(6,07)	253(6,30)	
	Co	343(6,17)	–	255(6,24)	
	Ni	–	334(5,97)	253(6,14)	
	Cu	–	336(6,32)	251(6,59)	
	Ag	–	335(6,07)	254(6,34)	
	Pb	–	291(6,19)	254(6,53)	
(Ic)		344(5,77)	333(5,74)	297(5,66)	252(5,83)
	Li	–	329(5,29)	291(5,34)	253(5,66)
	K	–	–	291(5,46)	253(5,79)
	Ga	–	326(5,25)	–	254(5,65)
	Co	343(5,53)	333(5,50)	–	252(5,66)
	Cu	–	319(5,34)	293(5,39)	253(5,73)
	Pb	–	329(5,30)	291(5,37)	254(5,69)

TABLE 3. Principal Characteristics and Comparison of Selectivity Coefficients of Pb-Selective Electrodes based on Compound (Ib) and a Known Electrode based on a Podand with Thioureide Groups (II) [3]

Electrode based on compound	Concentration range of electrode operation, M	Selectivity coefficients			Selectivity coefficients					
		Cd	Ni	Co	Zn	Cu	Ag	Li, Na, K, Pb, Cs, Ca, Sr	Ba	Mg
(Ib)	$1\cdot10^{-6}$–$1\cdot10^{-2}$	$3\cdot10^{-3}$	$7\cdot10^{-3}$	$5\cdot10^{-3}$	$3\cdot10^{-3}$	$3,6\cdot10^{-1}$	10	10^{-3}	$6,4\cdot10^{-4}$	$2,3\cdot10^{-3}$
(II)	$1\cdot10^{-5}$–$5\cdot10^{-2}$	$1\cdot10^{-1}$	$2\cdot10^{-2}$			$1,6\cdot10^{-2}$				

groups are found at 1295 cm^{-1}; of C=O, at 1683 cm^{-1}. The ether bonds C_{Ar}—O—C_{alk} appear at 1050-1070 and 1245-1250 cm^{-1}; C_{alk}—O—C_{alk}, at 1003 and 1150 cm^{-1}. The ν(Ar—H) of orthosubstituted benzene occurs at 750 cm^{-1}.

The ability of the synthesized compounds to form complexes was studied by electronic spectroscopy and extraction of metal picrates.

A bathochromic or hypsochromic shift of the absorption maxima and sometimes their disappearance are observed in electronic spectra of PD (Ia and b). This is due to the ability of these PD to form complexes selectively (Table 2).

Extraction of metal picrates [3] demonstrated that PD with 4-antipyryliminomethine groups form extractable complexes with 18 metal picrates: Li, Na, K, Cs, Ca, Sr, Ba, Mg, Ag, Ga, Mn, Co, Ni, Cu, Hg, Zn, La, Al, and Pb. The experimental data suggest that 27-30% of Ca^{2+}, Ag^{+}, Cu^{2+}, and Mn^{2+} can be extracted from water into $CHCl_3$ using the PD synthesized. Quantitative results showed that the selectivity of complexation depends on the length of the oxyethylene fragment. The ions K^{+}, Li^{+}, and Ca^{2+} are extracted best by PD (Ia); Ag^{+}, Cu^{+}, and Mn^{2+}, by PD (Ib); and Pb, by PD (Ic). It should be noted that 4-aminoantipyrine does not form extractable complexes with Li, Sr, Ba, Mn, Ni, Zn, or Pb picrates.

Podand (Ib) was tested as an electroactive substance in an ion-selective electrode for determining the Pb ion activity in aqueous solutions [4].

An electrode with PD (Ib) has a linear electrode function between Pb concentrations $1\cdot10^{-6}$-$1\cdot10^{-2}$ M with a slope of 22-24 mV/pPb. Table 3 presents the principal characteristics of the electrode based on PD (Ib). The electrode with PD (Ib) is not affected by H^{+} at pH 3.5-5.5. Comparison of the selectivity coefficients of the electrode based on the PD with 4-aminoantipyrine and that based on the PD with thioureide groups indicates that the electrode proposed in the present work is more sensitive for Pb^{2+}. It also can determine the Pb^{2+} activity more selectively in the presence of alkali and alkaline earth metals, Cd, Ni, and Co. This is very important for analysis of electrolytes, wastewaters from industrial plants, nonferrous metallurgy products, and other samples.

EXPERIMENTAL

UV spectra (Tables 1 and 2) were recorded on a Specord UV-Vis spectrometer (10^{-5} M in $CHCl_3$). IR spectra were taken on a UR-20 spectrophotometer between 400-4000 cm^{-1} as mineral oil mulls or KBr pellets. Elemental analyses and melting points are given in Table 1.

1,8-Bis[2-(4-antipyryliminomethine)phenoxy]-3-oxaoctane (Ia). 4-Aminoantipyrine (4 g, 1.968 mmoles) and 1,5-bis(oxybenzaldehyde)-3-oxapentane (3 g, 0.955 mmole) were dissolved in boiling ethanol (50 ml). After cooling to 18-20°C, the precipitate was filtered off and crystallized from ethanol as yellow needles.

1,8-Bis[2-(4-antipyryliminomethine)phenoxy]-3,6-dioxaoctane (Ib). 4-Aminoantipyrine (3.66 g, 1.80 mmoles) and 1,8-bis(oxybenzaldehyde)-3,6-dioxaoctane (4.322 g, 0.90 mmole) were dissolved in boiling ethanol (350 ml). Yellow needles were crystallized from ethanol.

1,11-Bis[2-(4-antipyryliminomethine)phenoxy]-3,6,9-trioxaundecane (Ic). 4-Aminoantipyrine (1.05 g, 0.52 mmole) and 1,11-bis(oxybenzaldehyde)-3,6,9-trioxaundecane (1 g, 0.25 mmole) were dissolved in boiling ethanol. The ethanol was removed. A dark oil was precipitated from the ethanol with ether. The oil solidified after drying under vacuum over P_2O_5 and paraffin. An ion-selective membrane was prepared from (Ib) by stirring it with a solution of polyvinylchloride (PVC) in THF and dibutylphthalate (DBP) as plastifier. Membrane composition: (Ib), 2%; PVC, 30%; DBP, 68%; remainder, THF. The solution obtained was poured into a Petri dish and dried for 24 h at ~20°C. The membrane obtained was kept for 24 h in $1\cdot10^{-2}$ M Pb nitrate.

The emf measurements were made on an Orion-901 pH meter. A EVL-1M3 silver chloride electrode was used as reference.

Quantitative determinations of Pb activity were made by placing the ion-selective and reference, for example, AgCl, electrodes in the solution to be analyzed and measuring the emf in mV.

A diagram of the measuring cell is

$$\mathrm{Ag}\,\Big|\,\mathrm{AgCl}\ \ 0{,}01\,M\ \mathrm{Pb(NO_3)_2}\,\Big|\,\textbf{Membrane}\,\Big|\,\begin{matrix}\textbf{Analyzed}\\ \textbf{solution}\end{matrix}\,\Big|\,\begin{matrix}0{,}1\ M\\ \mathrm{KNO_3}\end{matrix}\,\Big|\,\begin{matrix}0{,}1\ M\\ \mathrm{KCl}\end{matrix}\ \mathrm{AgCl}\,\Big|\,\mathrm{Ag}$$

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REACTION OF 2-(4-ALKYLPIPERAZINO)-3-CHLORO-1,4-NAPHTHOQUINONES WITH SODIUM AZIDE

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It was shown that 2-(4-alkylpiperazino)-3-chloro-1,4-naphthoquinones react on heating with NaN_3 in DMF to form new heterocyclic quinones — 1,2,3,4-tetrahydro-13-alkyl-3,1-(iminoethano)benzo[g]quinoxaline-5,10-diones as well as the corresponding 2-(4-alkylpiperazino)-3-aminonaphthoquinones and naphthimidazopyrazinediones.

It is known that 2-morpholino- and 2-piperidino-3-chloro-1,4-naphthoquinones react on heating with NaN_3 in DMF with the formation of the corresponding 3-amino derivatives and naphth[2',3':4,5]imidazo-6,11-diones [1]. The precursors of the latter, as has been shown with the example of 2-(4-acylpiperazino)-3-azido-1,4-naphthoquinones, are dehydrogenation products of the piperazine ring — enaminonaphthoquinones [2]. In continuation of these investigations, the reaction of NaN_3 with 2-(4-alkylpiperazino)-3-chloro-1,4-naphthoquinones (Ia-c) was carried out in DMF at 80°C, and it was found that unlike 2-(4-acylpiperazino)-naphthoquinones [2], the reaction produced, besides the 3-amino derivatives (IIIa-c) and 2-alkyl-1,2,3,4-tetrahydronaphth[2',3':4,5]imidazo[1,2,a]pyrazine-6,11-diones (IVa-c), new heterocyclic compounds — 1,2,3,4-tetrahydro-13-alkyl-3,1(iminoethano)benzo[g]quinoxaline-5,5-diones (Va-c) (see Scheme 1). The yield of the reaction products is given in Table 1.

The thermolysis of azide (IIa), which separated out on reacting compound (Ia) with NaN_3 at 20°C leads to the same set of products (IIIa)-(Va).

It can be assumed that, like naphthimidazopyrazinediones (IV), the (3,1-iminoethano)-benzoquinoxaline derivatives (Va-c) are products of the intramolecular cyclization of the intermediately formed unstable enaminonaphthoquinones (A). Attempts to isolate them, unlike 4-acylpiperazino-substituted naphthoquinones [2], were unsuccessful as could be expected [3]. The direction of the cyclization of 1-(3-amino-1,4-naphtho-2-quinolyl)-4R-tetrahydropyrazines of type (A) is clearly influenced by the character of the substituent in the partially hydrogenated pyrazine ring: in the presence of an acyl group, the attack of the amine proceeds at the nearest α-carbon atom at the double bond with the formation of an imidazole ring [2], while in the presence of an alkyl group (R), the reaction occurs at the α- and β-carbon atoms with the formation of both five-membered (IV) and six-membered (V) rings.

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