

CALCIUM TETRA(4-CHLOROPHENYL) BORATE COMPLEXES OF SOME NEW MACROCYCLIC POLYETHERDIAMIDES AND THEIR MEMBRANE SELECTIVITY

Jaromír PETRÁNEK and Olen RYBA

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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Preparation of some new macrocyclic polyetherdiamides and their complexes with calcium and tetra(4-chlorophenyl) borate is described. The selectivities of these compounds for calcium with respect to ions of the other alkaline earth and alkali metals in poly(vinyl chloride) membranes plasticized with 2-nitro-1-octyloxybenzene are compared.

Recently, we have found¹ that macrocyclic polyetherdiamides form ternary ion-associated complexes with calcium cations and tetra(4-chlorophenyl)borate anions, and that these complexes can be isolated as crystalline compounds of defined composition. They may be used as active components in membranes of calcium ion-selective electrodes. The membrane selectivity of these complexes differs markedly from that of membranes with free ligands. The use of complexes has a favourable effect, especially in raising the selectivity for calcium with respect to alkali metals. In connection with the investigation of the effects of structure of macrocyclic polyetherdiamides on their membrane selectivity, preparation of some new diamides and their complexes with calcium and tetra(4-chlorophenyl)borate is reported in this study. The study is also concerned with the selectivity of these compounds for calcium with respect to ions of the other alkaline earth and alkali metals in their application in poly(vinyl chloride) membranes.

EXPERIMENTAL

Melting points were determined with a Kofler hot stage. ¹H NMR spectra were recorded in deuteriochloroform (tetramethylsilane as the internal standard) with a Jeol PS-100 apparatus at 100 MHz. Chemical shifts are given in δ (ppm). Mass spectra were recorded with an AEI-MS 902 spectrometer; the most important ions are given in *m/e* values. Elemental analyses were performed with a CHN Perkin-Elmer 240 analyzer.

Starting Materials

Dicarboxylic acids used in the preparation of macrocyclic diamides were prepared by reacting 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,4-butanediol, *trans*-1,2-cyclohexanediol, 2,3-

-butanediol and 2,3-dimethyl-2,3-butanediol with ethyl diazo acetate, which was followed by hydrolysis using a procedure described earlier^{1,2}. Chlorides of these acids were prepared by a reaction with thionyl chloride according to ref.³, each time before the cyclization.

N,N'-Dibenzyl-1,11-diamino-3,6,9-trioxaundecane dihydrochloride was prepared according to ref.². N,N'-Dioctyl-1,11-diamino-3,6,9-trioxaundecane dihydrochloride obtained by a similar procedure had a m.p. 218–223°C. For C₂₄H₅₄Cl₂N₂O₃ (489.6), calculated: 58.87% C, 11.12% H, 5.72% N; found: 58.94% C, 11.30% H, 5.76% N. Free bases used in the cyclization reaction were obtained by alkalizing the aqueous solution of hydrochloride and extraction with benzene.

Cyclic Diamides

Polyetherdiamides I–VI were prepared by a reaction between benzene solutions of the respective chlorides of dicarboxylic acids with the corresponding derivatives of 1,11-diamino-3,6,9-trioxaundecane under conditions of high dilution². The products were purified chromatographically on a silicagel column (Kieselgel 60; 0.2–0.5 mm Fluka) using a benzene-methanol mixture (5 : 1) as the eluent. Purity of the final products was checked by TLC chromatography on silicagel G (Merck) with detection by Dragendorff's reagent. All the polyetherdiamides described below were obtained as viscous oils.

8,20-Dibenzyl-8,20-diaza-1,5,11,14,17-pentaoxacyclodocosane-7,21-dione (I): 52%. ¹H NMR: 1.88 (m, 2 H, CH₂); 3.35–3.75 (20 H, NCH₂, CH₂O, CH₂OCH₂CH₂); 4.22 (bs, 4 H, OCH₂CO); 4.66 (bs, 4 H, CH₂Ar); 7.2 (s, 10 H, Ar). Mass spectrum: 528 (M⁺), 500, 485, 427, 192, 190, 176. For C₂₉H₄₀N₂O₇ (528.6), calculated: 65.89% C, 7.63% H, 5.29% N; found: 65.93% C, 7.77% H, 5.17% N.

8,20-Dibenzyl-3,3-dimethyl-8,20-diaza-1,5,11,14,17-pentaoxacyclodocosane-7,21-dione (II): 43%. ¹H NMR: 0.88 (s, 6 H, CH₃); 3.28 (s, 4 H, OCH₂CCH₂O); 3.4–3.75 (16 H, NCH₂, CH₂.OCH₂CH₂); 4.24 (bs, 4 H, OCH₂CO); 4.66 (bs, 4 H, CH₂Ar); 7.2 (s, 10 H, Ar). Mass spectrum: 556 (M⁺), 528, 513, 427, 278, 192, 190, 176. For C₃₁H₄₄N₂O₇ (556.7), calculated: 66.88% C, 7.97% H, 5.03% N; found: 66.88% C, 8.08% H, 4.92% N.

9,21-Dibenzyl-9,21-diaza-1,6,12,15,18-pentaoxacyclotricosane-8,22-dione (III): 60%. ¹H NMR: 1.72 (m, 4 H, CH₂); 3.35–3.75 (20 H, NCH₂, CH₂O, CH₂OCH₂CH₂); 4.22 (bs, 4 H, OCH₂CO); 4.68 (bs, 4 H, CH₂Ar); 7.2 (s, 10 H, Ar). Mass spectrum: 542 (M⁺), 514, 500, 427, 264, 262, 192, 190, 176. For C₃₀H₄₂N₂O₇ (542.7), calculated: 66.39% C, 7.80% H, 5.16% N; found: 66.36% C, 7.93% H, 4.85% N.

5,17-Dibenzyl-5,17-diaza-2,8,11,14,20-pentaoxabicyclo[19,4,0]pentacosane-4,18-dione (IV): 55%. ¹H NMR: 1.0–2.4 (8 H, CH₂-cyclohexyl); 3.15–3.7 (18 H, NCH₂, CH₂OCH₂CH₂, OCH); 4.36 (bs, 4 H, OCH₂CO); 4.68 (bs, 4 H, CH₂Ar); 7.2 (s, 10 H, Ar). Mass spectrum: 568 (M⁺), 525, 511, 487, 472, 429, 427, 396, 378, 323, 307, 298, 238, 192. For C₃₂H₄₄N₂O₇ (568.7), calculated: 67.58% C, 7.80% H, 4.92% N; found: 67.66% C, 7.78% H, 4.63% N.

2,3-Dimethyl-7,19-dioctyl-7,19-diaza-1,4,10,13,16-pentaoxacycloheneicosane-6,20-dione (V): 52%. ¹H NMR: 0.86 (t, 6 H, CH₃-octyl); 1.15 (d, 6 H, CH₃); 1.25–1.7 (24 H, CH₂-octyl); 3.15 to 3.75 (20 H, NCH₂, NCH₂-octyl, CH₂OCH₂CH₂); 4.26 (bs, 6 H, OCH₂CO, OCH). Mass spectrum: 586 (M⁺), 544, 543, 473, 471, 459, 392, 346, 286, 284, 242, 240, 214. For C₃₂H₆₂N₂O₇ (586.8), calculated: 65.49% C, 10.64% H, 4.77% N; found: 65.15% C, 10.56% H, 4.50% N.

2,2,3,3-Tetramethyl-7,19-dioctyl-7,19-diaza-1,4,10,13,16-pentaoxacycloheneicosane-6,20-dione (VI): 43%. ¹H NMR: 0.84 (t, 6 H, CH₃-octyl); 1.2–1.6 (36 H, CH₃, CH₂-octyl); 3.2–3.7 (20 H, NCH₂, NCH₂-octyl, CH₂OCH₂CH₂); 4.18 (bs, 4 H, OCH₂CO). Mass spectrum: 614 (M⁺), 556, 531, 513, 473, 471, 360, 343, 329, 320. For C₃₄H₆₆N₂O₇ (614.9), calculated: 66.41% C, 10.82% H, 4.55% N; found: 65.91% C, 10.88% H, 4.34% N.

Complexes of Cyclic Diamides with Calcium Tetra(4-chlorophenyl) Borate

Potassium tetra(4-chlorophenyl) borate (0.2 mmol) dissolved in 1 ml of methanol was added to a solution of polyetherdiamide (0.2 mmol) and calcium thiocyanate (0.1 mmol) in 1 ml of methanol. The precipitated complex was isolated by filtration, washed with a small amount of cold methanol, and dried. In some cases the complex separated as oil which crystallized after several hours. The yields varied between 60–75%. The following complexes were prepared (tetra(4-chlorophenyl) borate anion being denoted as A):

2I.Ca.2A: m.p. 236–244°C. For $C_{106}H_{112}B_2CaCl_8N_4O_{14}$ (2 011.5), calculated: 63.29% C, 5.61% H, 2.79% N, 14.10% Cl; found: 63.17% C, 5.67% H, 2.74% N, 14.12% Cl.

2II.Ca.2A: m.p. 197–199°C. For $C_{110}H_{120}B_2CaCl_8N_4O_{14}$ (2 067.6), calculated: 63.90% C, 5.85% H, 2.71% N, 13.72% Cl; found: 63.88% C, 5.93% H, 2.84% N, 13.54% Cl.

2III.Ca.2A: m.p. 173–175°C. For $C_{107}H_{114}B_2CaCl_8N_4O_{14}$ (2 025.5) calculated: 63.45% C, 5.67% H, 2.76% N, 14.00% Cl; found: 63.56% C, 5.77% H, 2.71% N, 14.02% Cl.

2IV.Ca.2A: m.p. 108–110°C. For $C_{112}H_{120}B_2CaCl_8N_4O_{14}$ (2 091.6) calculated: 64.31% C, 5.78% H, 2.68% N; found: 64.14% C, 5.91% H, 2.51% N.

2V.Ca.2A: m.p. 49–51°C. For $C_{112}H_{156}B_2CaCl_8N_4O_{14}$ (2 127.9) calculated: 63.22% C, 7.39% H, 2.63% N; found: 63.27% C, 7.36% H, 2.72% N.

2VI.Ca.2A: m.p. 128–132°C. For $C_{116}H_{164}B_2CaCl_8N_4O_{14}$ (2 184.0) calculated: 63.79% C, 7.56% H, 2.56% N, 12.98% Cl; found: 63.74% C, 7.75% H, 2.63% N, 12.63% Cl.

Preparation of Membranes and EMF Measurement

The membranes were prepared by employing a technique described earlier¹. The composition of the membranes was: 0.7% polyetherdiamide, 66.2% 2-nitro-1-octyloxybenzene, 33.1% poly(vinyl chloride), or 1.6% of a complex of cyclic diamide (*cf.* the preceding paragraph), 65.6% 2-nitro-1-octyloxybenzene, 32.8% poly(vinyl chloride). For EMF measurements the membranes were incorporated into the electrode body Philips type IS 561 using 0.01M-CaCl₂ as the internal filling solution. All measurements were carried out at 25°C using an Ionalyzer 901 (Orion) apparatus and cells of the following type: Hg; Hg₂Cl₂, KCl (satd.)/0.1M-NH₄NO₃/measured solution/membrane/0.01M-CaCl₂, AgCl; Ag. The selectivity coefficients were obtained by the separate solutions method in 0.1M chloride solutions as has been described in detail in an earlier paper².

RESULTS AND DISCUSSION

New macrocyclic polyetherdiamides *I–VI* with a structurally modified group X in the dioxadiacyl part of the macrocycle were prepared. With calcium ions and tetra(4-chlorophenyl) borate anions, all these polyetherdiamides yield crystalline complexes insoluble in water, alcohol, and benzene. The stoichiometric composition of these complexes is two ligands and two tetra(4-chlorophenyl)borate anions per one calcium cation. Ion-selective properties of the complexes were examined electrochemically. The complexes were incorporated into membranes made of poly(vinyl chloride) plasticized with 2-nitro-1-octyloxybenzene. In order to detect structural effects and changes caused by complexation, free ligands were also measured under

by one carbon atom. In this case, a satisfactory selectivity for calcium is still preserved. Substitution of the central carbon atom in the bridge by two methyl groups in the case of *II* slightly improves the Ca/Ba selectivity, with lithium being preferred at the same time. This effect resembles that observed in the substitution of the bridge containing two carbon atoms with four methyl groups. The membrane selectivity of complexes of diamides *I* and *II* for calcium with respect to barium remains unchanged, that with respect to alkali metals is markedly improved. Extension of the bridge to contain four carbon atoms in *III* generally impairs selectivity of both the free ligand and its complex. The ether oxygen atoms of the acyl part of the macrocycle in *IV* are joined by two carbon atoms which are part of the cyclohexane ring and thus have their mutual position fixed to a considerable extent. This is obviously the cause underlying the good selectivity properties of this ligand for calcium with respect to strontium, barium, and alkali metals. The membrane selectivity becomes better still in the complex of this diamide which ranks among the best ionophores for calcium of this type.

V and *VI* are analogs of macrocyclic polyetherdiamides described earlier¹ in which benzyl substituents of the amide nitrogen were replaced with octyl groups. The membrane selectivity of these compounds and their complexes remains virtually unaffected by this change. Compared with benzyl derivatives, in membranes containing these compounds the effect of changes in hydrodynamic conditions on the stability of electrode potential is reduced to minimum.

TABLE II

Membrane selectivity coefficients of complexes of polyetherdiamides with calcium and tetra-4-chlorophenyl borate (A) expressed as $-\log k_{Ca,M}$

Ion	Complex 2(I-VI).Ca.2A					
	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>
Mg ²⁺	3.19	4.45	3.80	4.40	4.20	3.88
Sr ²⁺	0.77	1.49	0.90	1.60	0.95	0.75
Ba ²⁺	1.09	1.78	0.67	1.74	1.10	1.49
Li ⁺	1.51	2.14	2.06	2.87	2.38	1.53
Na ⁺	2.46	3.40	2.06	3.63	3.28	3.23
K ⁺	2.02	3.05	1.55	3.82	3.48	3.36
Rb ⁺	2.14	3.25	1.97	4.00	3.62	3.64
Cs ⁺	1.45	3.24	1.85	4.31	3.73	3.88

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