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Three types of silicon podands, $Me_2Si(OR)_2$, $EtSi(OR)_3$ and $PhSi(OR)_3$, where R is a polyoxaethylene chain with different numbers of oxygen atoms (two, three or four), were obtained and studied by ^{1}H, ^{13}C and ^{29}Si NMR methods. NMR spectra of ^{1}H, ^{7}Li, ^{13}C, ^{23}Na and ^{29}Si nuclei were also used for the study of lithium, sodium and rubidium complexes with the silicon podands. Theoretical calculations were performed using the PM3 hamiltonian. The heats of reactions between the compounds obtained and $SbCl_5$ were determined.

Keywords: Podand solvent; NMR method; Heat of reaction; Theoretical calculation

INTRODUCTION

Various inorganic esters of ethylene glycol have been prepared as described previously [1]. In previous papers [2–4] we have also demonstrated that ligands including poly(oxaalkyl) chains formed proton or cation channels in which the cations showed a high cation polarizability, as a result of the so-called Zundel polarizability [5].

In the past few years we have been interested in di- and tripodands, characterized by the diverse central atom, such as B, P, S or Si. NMR is known to be a very useful method for the investigation of supramolecular complexes with metal ions in solutions. We studied the ligands and their complexes with various metal cations, and neutral molecules ($SbCl_5$), by using NMR, FTIR and UV spectroscopy, and calorimetric and kinetic methods. Some of the new podands we used as solvents in organic reactions (proton or acyl transfer) were studied by kinetic methods [6–13].

Results concerning two silicon podand solvents, phenyl-tris(1,4-dioxapentyl)silane (PhSi23) and ethyl-tris(1,4-dioxapentyl)silane (EtSi23), were published recently [14,15]. These compounds and their complexes were studied by FTIR, multinuclear NMR, electronic and semi-empirical methods. The results were very promising and led us to continue our studies of new silicon podand solvents.

EXPERIMENTAL

General Method of Synthesis of Silicon Podands

Three types of silicon podands were obtained by the following reaction:

$$(R)_m - SiCl_{4-m} + (4-m)\,CH_3(OCH_2CH_2)_nOH]$$

$$\rightarrow (R)_m - Si[(OCH_2CH_2)_nOCH_3]_{4-m} + (4-m)HCl$$

where $R = CH_3$, C_2H_5, Ph; $m, n = 1-3$.

Anhydrous polyethylene glycol was cooled to about 0°C and chlorosilane added dropwise very slowly with continuous stirring. The mixture was then heated to boiling and kept at this temperature for about 5 h (until emission of gaseous HCl had ceased); the product was distilled under pressure (10 mmHg). The ratio between the glycols and chlorosilanes used in the reaction depends on the type of podand, but in every case it had to be a small molar excess of glycol.

NMR Measurements

The NMR spectra were recorded in CD_3CN on a Varian Gemini 300 MHz spectrometer. All spectra were locked to deuterium resonance of CD_3CN.

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TABLE I Boiling points and yields of products

Podand	Short name	Yield (%)	Boiling point (°C/mmHg)
$(CH_3)_2Si(OCH_2CH_2OCH_3)_2$	Me_2Si22	43	95/10
$(CH_3)_2Si[(OCH_2CH_2)_2OCH_3]_2$	Me_2Si32	40	150–165/10
$(CH_3)_2Si[(OCH_2CH_2)_3OCH_3]_2$	Me_2Si42	44	215/10
$C_2H_5Si(OCH_2CH_2OCH_3)_3$	EtSi23	77	113–115/10
$C_2H_5Si\ [(OCH_2CH_2)_2OCH_3]_3$	EtSi33	68	210–230/10
$C_2H_5Si[(OCH_2CH_2)_3OCH_3]_3$	EtSi43	45	270–280/10
$PhSi(OCH_2CH_2OCH_3)_3$*	PhSi23	92	181–183/1.2
$PhSi\ [(OCH_2CH_2)_2OCH_3]_3$*	PhSi33	90	245–247/1.1
$PhSi[(OCH_2CH_2)_3OCH_3]_3$*	PhSi43	85	255–258/0.2

*Ref. [8].

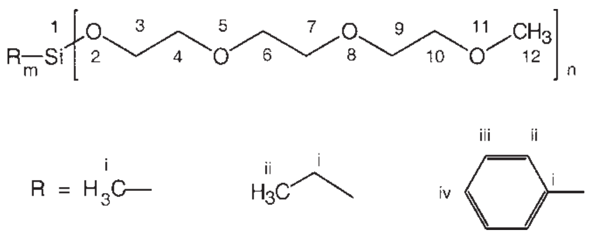


FIGURE 1 Atomic numbering used for the molecules studied.

^1H NMR measurements were carried out at an operating frequency of 300.075 MHz; flip angle (pw) = 45°; spectral width (sw) = 4500 Hz; acquisition time (at) = 2.0 s; relaxation delay (d1) = 1.0 s; $T = 293$ K; and TMS as internal standard No window function or zero filing was used. Digital resolution = 0.2 Hz/point. ^{13}C NMR spectra were recorded at the operating frequency 75.454 MHz; pw = 60°; sw = 19000 Hz; at = 1.8 s, d1 = 1.0 s; $T = 293$ K; and TMS as the internal standard. Line boarding parameters were 0.5 or 1 Hz.

The following parameters were used for ^7Li NMR: LiCl in D_2O ($1\ mol\ dm^{-3}$) as external standard, sfrq = 116.619 MHz, pw = 70°, sw = 6000 Hz, at = 3 s, d1 = 0.5 s; $T = 293$ K. Digital resolution = 0.6 Hz/point. No window function or zero filing was used.

^{29}Si NMR spectra were recorded using the following parameters: sfrq = 59.611 MHz, pw = 60°, sw = 10000 Hz, at = 4 s, d1 = 1.5 s, $T = 293$ K; and TMS in CD_3Cl ($1\ mol\ dm^{-3}$) as external standard Digital resolution = 0.3 Hz/point. No window function or zero filing was used.

TABLE II ^1H Chemical shifts for silicon podands in CD_3CN at 293 K

	^1H Chemical shift (ppm)										
Podand	H^3	H^4	H^6	H^7	H^9	H^{10}	CH_3	H^i	H^{ii}	H^{iii}	H^{iv}
Me_2Si22	3.73 (t)	3.39 (t)	–	–	–	–	3.28 (s)	0.06 (s)	–	–	–
Me_2Si32	3.73 (t)	3.47 (t)	3.42 (t)	3.53 (t)	–	–	3.26 (s)	0.02 (s)	–	–	–
Me_2Si42	3.62 (t)	3.37 (t)	3.42–3.50 (m)		3.32 (t)	3.21 (s)	0.07 (s)	–	–	–	
EtSi23	3.78 (t)	3.37 (t)	–	–	–	–	3.25 (s)	0.55 (q)	0.87 (t)	–	–
EtSi33	3.65 (t)	3.51 (t)	3.57 (t)	3.44 (t)	–	–	3.28 (s)	0.57 (q)	0.90 (t)	–	–
EtSi43	3.68 (t)	3.37 (t)	3.40–3.50 (m)		3.32 (t)	3.28 (s)	0.55 (q)	0.77 (t)	–	–	
PhSi23	3.91 (t)	3.46 (t)	–	–	–	–	–	3.29 (s)	7.65 (d)	7.40 (t)	7.47 (t)
PhSi33	3.92 (t)	3.52–3.55 (m)		3.45 (t)	–	–	3.28 (s)	–	7.70 (d)	7.41 (t)	7.47 (t)
PhSi43	3.92 (t)	3.52–3.59 (m)				3.45 (t)	3.28 (s)	–	7.68 (d)	7.40 (t)	7.42 (t)

s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet.

TABLE III ^{13}C Chemical shifts for silicon podands in CD_3CN at 293 K

	^{13}C Chemical shifts (ppm)										
Podand	C^3	C^4	C^6	C^7	C^9	C^{10}	C^{12}	C^i	C^{ii}	C^{iii}	C^{iv}
Me_2Si22	61.48	73.61	58.66	–	–	–	–	−3.46	–	–	–
Me_2Si32	61.32	72.10	70.19	71.63	58.61	–	–	−3.50	–	–	–
Me_2Si42	61.24	72.10	70.06; 69.95		70.04	71.38	58.34	−3.68	–	–	–
EtSi23	61.69	73.69	58.48	–	–	–	–	1.75	5.93	–	–
EtSi33	61.61	71.87	70.02	71.51	58.48	–	–	1.58	5.98	–	–
EtSi43	61.47	71.69	69.96; 69.89		70.02	71.32	58.29	1.45	5.74	–	–
PhSi23	63.99	75.02	59.63	–	–	–	–	132.51	136.61	129.74	132.39
PhSi33	64.20	73.62	73.32	71.83	59.71	–	–	131.07	136.75	129.75	132.42
PhSi43	64.23	73.65	71.98; 72.03		71.85	73.44	59.68	132.54	136.75	129.78	132.42

TABLE IV ^{29}Si Chemical shifts for silicon podands in CD_3CN at 293 K

Podand	^{29}Si Chemical shift (ppm)
Me_2Si22	− 43.78
Me_2Si32	− 45.22
Me_2Si42	− 45.39
EtSi23	− 60.28
EtSi33	− 60.76
EtSi43	− 61.02
PhSi23	− 65.32
PhSi33	− 65.99
PhSi43	− 66.12

The stability constants of the complexes were estimated according to the Benesi–Hildebrand method [16].

Semiempirical Calculations

PM3 semiempirical calculations were performed by using the WINMOPAC V2.0 program [17, 18]. In all cases the precise keyword was used and full geometry optimization was carried out without any symmetry constraints [17, 18].

Calorimetric Measurements

Heats of reaction were determined following the procedure given in [19] and [20] by the titration of podand compounds with $SbCl_5$ dissolved in CCl_4.

RESULTS AND DISCUSSION

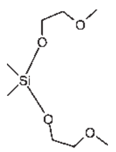
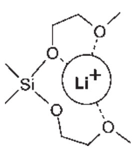
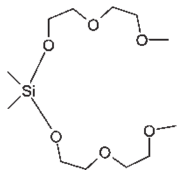
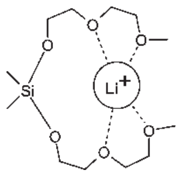
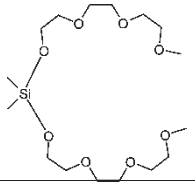
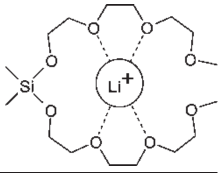
We obtained two groups of podands (di- and tripodands) in which the silicon atom was the central atom of the molecule. The dimethyl Si-ligands belonged to the dipodands while both Ph and Et Si-ligands were in the tripodand group. The structures, boiling points and yields for the podands are given in Table I. The numbering of atoms in the molecules is presented in Fig. 1.

^{1}H, ^{13}C and ^{29}Si NMR data for the silicon podands are given in Tables II–IV, respectively The ^{1}H, ^{13}C and ^{29}Si NMR spectra correspond to the structures of the arrangements studied and are very important with regard to results of Si-ligand complexes with metal cations. In ^{1}H and ^{13}C NMR data fundamental changes in connection with the length of the podand chain are not observed, while for ^{29}Si NMR spectra these influences are considerable and are connected with an increase in induction effect.

Tables V–VII include results of the PM3 hamiltonian calculations of the Si-podands and theirs complexes with the lithium cation. Values for the heat of formation (ΔF) of 1:1 complexes with the Li^+ ion are approximately 500 kJ mol^{-1} greater than those for the free ligands. Differences in ΔF between complexes and ligands provide evidence that the complexation processes for all cases are similar. Ligands in complexes are well organized because of the cation. The dipole moments of the relative complexes are greater than for the free ligands. The effect of the interaction between the lithium cation and oxygen atoms of the polyoxaethylene ligand chains is to decrease the partial charge on the oxygen atoms that participate in complexation, and this was observed, while for noncomplexing oxygen atoms the partial charges increase. These facts allow us to understand the method of complexation.

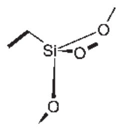
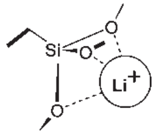
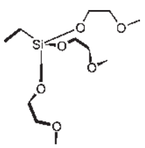
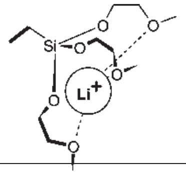
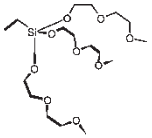
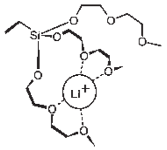
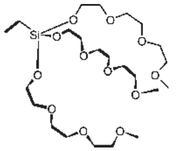
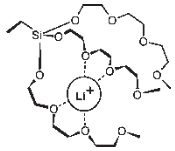
^{1}H and ^{13}C chemical shifts for 1:1 complexes of Si-podands with lithium, sodium and rubidium ions in deuterium acetonitryl solutions are presented in Tables VIII and IX. In all cases small changes

TABLE V Some theoretical parameters for double-chain silanes

						
ΔF (kJ mol^{-1})	− 1062.41577	− 603.50808	− 1386.20097	− 916.42530	− 1709.98207	− 1292.19889
Dipole moment (D)	0.37990	3.64445	0.82610	3.57566	0.37446	3.13173
HOMO energy (eV)	− 9.600	− 13.336	− 9.637	− 12.523	− 9.648	− 12.960
LUMO energy (eV)	0.937	− 3.347	0.899	− 3.240	0.890	− 2.543
			Charge for O-atoms			
O^2	− 0.4072	− 0.4144	− 0.4068	− 0.4300	− 0.4072	− 0.3400
	− 0.4072	− 0.3751	− 0.4068	− 0.4389	− 0.4072	− 0.3428
O^5	− 0.2724	− 0.2102	− 0.2762	− 0.2098	− 0.2755	− 0.1980
	− 0.2724	− 0.2167	− 0.2762	− 0.2095	− 0.2755	− 0.1722
O^8			− 0.2673	− 0.2037	− 0.2715	− 0.1892
			− 0.2673	− 0.2069	− 0.2715	− 0.1761
O^{11}					− 0.2674	− 0.2833
					− 0.2674	− 0.2783

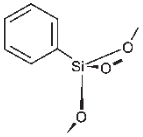
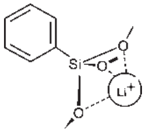
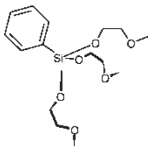
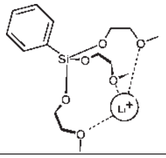
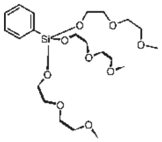
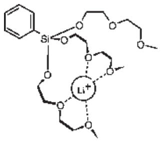
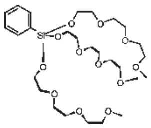
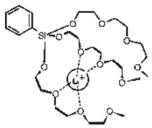
ΔF, heat of formation.

TABLE VI Some theoretical parameters for triple-chain silanes with an Et group

								
ΔF (kJ mol^{-1})	−1037.06662	−532.70329	−1535.06662	−1029.16523	−2021.09623	−1515.17689	−2506.64796	−2054.36213
Dipole moment (D)	0.88922	4.11495	0.71962	4.07827	0.77070	3.78047	0.76796	3.41936
HOMO energy (eV)	−9.467	−13.307	−9.548	−12.313	−9.604	−12.140	−9.616	−12.396
LUMO energy (eV)	0.950	−3.934	0.813	−3.689	0.758	−3.536	0.744	−3.047
Charge for O-atoms								
O^2	−0.4429	−0.4315	−0.4474	−0.4294	−0.4474	−0.4505	−0.4477	−0.4312
	−0.4052	−0.3999	−0.4474	−0.4631	−0.4107	−0.4571	−0.4110	−0.3848
	−0.4430	−0.3961	−0.4112	−0.4503	−0.4474	−0.4326	−0.4477	−0.4284
O^5			−0.2723	−0.2307	−0.2732	−0.2395	−0.2756	−0.2229
			−0.2695	−0.2296	−0.2763	−0.2354	−0.2726	−0.1942
			−0.2723	−0.2372	−0.2763	−0.2336	−0.2757	−0.2073
O^8					−0.2676	−0.2757	−0.2718	−0.2772
					−0.2683	−0.2750	−0.2723	−0.2858
					−0.2676	−0.2749	−0.2718	−0.2451
O^{11}							−0.2674	−0.2659
							−0.2673	−0.2638
							−0.2674	−0.2747

ΔF, heat of formation.

TABLE VII Some theoretical parameters for triple-chain silanes with a Ph group head

								
ΔF (kJ mol^{-1})	−876.10687	−258.77126	−1375.76446	−858.98009	−1874.25344	−1394.95176	−2387.23561	−1870.12957
Dipole moment (D)	1.57271	3.52962	1.40884	3,42075	1.36571	3.38694	1.26653	3.23976
HOMO energy (eV)	−9.409	−11.683	−9.426	−11.473	−9.597	−11.926	−9.433	−11.922
LUMO energy (eV)	0.458	−4.847	0.386	−3.464	0.215	−3.043	0.407	−3.356
Charge for O-atoms								
O^2	−0.4345	−0.4419	−0.4291	−0.4447	−0.4283	−0.4226	−0.4208	−0.3820
	−0.4345	−0.4420	−0.4259	−0.4426	−0.4483	−0.3688	−0.4434	−0.4199
	−0.4345	−0.4436	−0.4296	−0.4459	−0.4291	−0.4155	−0.4155	−0.4254
O^5			−0.2637	−0.2379	−0.2705	−0.2246	−0.2582	−0.2745
			−0.2635	−0.2383	−0.2682	−0.2005	−0.2617	−0.2193
			−0.2634	−0.2379	−0.2711	−0.2040	−0.2687	−0.2295
O^8					−0.2658	−0.2641	−0.2716	−0.2814
					−0.2671	−0.2538	−0.2721	−0.2636
					−0.2652	−0.2577	−0.2714	−0.2696
O^{11}							−0.2655	−0.2631
							−0.2646	−0.2654
							−0.2691	−0.2820

ΔF, heat of formation.

TABLE VIII ^{1}H Chemical shifts for complexes (1:1) of Si podands with alkali metal cations

		^{1}H Chemical shifts (ppm)										
		H^3	H^4	H^6	H^7	H^9	H^{10}	CH_3	H^i	H^{ii}	H^{iii}	H^{iv}
Me_2Si22	Li^+	3.87 (t)	3.42 (t)	–	–	–	–	3.29 (s)	0.07 (s)	–	–	–
	Na^+	3.85 (t)	3.41 (t)	–	–	–	–	3.28 (s)	0.07 (s)	–	–	–
	Rb^+	3.79 (t)	3.35 (t)	–	–	–	–	3.27 (s)	0.07 (s)	–	–	–
Me_2Si32	Li^+	3.84 (t)	3.53–3.61 (m)			–	–	3.28 (s)	0.04 (s)	–	–	–
	Na^+	3.83 (t)	3.55–3.61 (m)			–	–	3.28 (s)	0.04 (s)	–	–	–
	Rb^+	3.80 (t)	3.56–3.60 (s)			–	–	3.27 (s)	0.03 (s)	–	–	–
Me_2Si42	Li^+	3.85 (t)	3.45–3.58 (m)					3.22 (s)	0.08 (s)	–	–	–
	Na^+	3.83 (t)	3.52–3.60 (m)					3.23 (s)	0.08 (s)	–	–	–
	Rb^+	3.80 (t)	3.48–3.58 (m)					3.22 (s)	0.07 (s)	–	–	–
EtSi23	Li^+	3.88 (t)	3.43 (t)	–	–	–	–	3.28 (s)	0.57 (q)	0.88 (t)	–	–
	Na^+	3.86 (t)	3.41 (t)	–	–	–	–	3.28 (s)	0.57 (q)	0.88 (t)	–	–
	Rb^+	3.82 (t)	3.39 (t)	–	–	–	–	3.26 (s)	0.55 (q)	0.87 (t)	–	–
EtSi33	Li^+	3.75 (t)	3.56–3.63 (m)			–	–	3.30 (s)	0.58 (q)	0.91 (t)	–	–
	Na^+	3.78 (t)	3.58–3.60 (m)			–	–	3.30 (s)	0.58 (q)	0.90 (t)	–	–
	Rb^+	3.71 (t)	3.50–3.57 (m)			–	–	3.29 (s)	0.57 (q)	0.90 (t)	–	–
EtSi43	Li^+	3.79 (t)	3.41–3.59 (m)			3.30 (s)	0.56 (q)	0.78 (t)	–	–		
	Na^+	3.80 (t)	3.42–3.58 (m)			3.30 (s)	0.56 (q)	0.78 (t)	–	–		
	Rb^+	3.76 (t)	3.40–3.55 (m)			3.29 (s)	0.55 (q)	0.77 (t)	–	–		
PhSi23	Li+	3.98 (bt)	3.60 (bt)	–	–	–	–	3.35 (s)	–	7.70 (d)	7.40 (t)	7.48 (t)
	Na^+	3.95 (t)	3.52 (t)	–	–	–	–	3.34 (s)	–	7.69 (d)	7.40 (t)	7.47 (t)
	Rb^+	3.94 (t)	3.52 (t)	–				3.34(s)		7.67 (d)	7.40 (t)	7.47 (t)
PhSi33	Li^+	4.05 (bs)	3.60–3.85 (m)		3.55 (t)	–	–	3.32 (s)	–	7.71 (d)	7.41 (t)	7.47 (t)
	Na^+	4.00 (t)	3.60–3.68 (m)		3.48 (t)	–	–	3.30 (s)	–	7.70 (d)	7.40 (t)	7.47 (t)
	Rb^+	4.01 (t)	3.60–3.65 (m)		3.48 (t)	–	–	3.29 (s)	–	7.70 (d)	7.40 (t)	7.47 (t)
PhSi43	Li^+	4.05 (bt)	3.55–3.80 (m)		3.38 (s)	–	7.70 (d)	7.40 (t)	7.43 (t)			
	Na^+	4.02 (t)	3.52–3.75 (m)		3.33 (s)	–	7.69 (d)	7.40 (t)	7.43 (t)			
	Rb^+	4.03 (bt)	3.55–3.75 (m)		3.33 (s)	–	7.70 (d)	7.40 (t)	7.42 (t)			

s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet.

TABLE IX ^{13}C Chemical shifts for complexes (1:1) of Si podands with alkali metal cations

		^{13}C Chemical shifts for Si podands (ppm)										
		C^3	C^4	C^6	C^7	C^9	C^{10}	C^{12}	C^i	C^{ii}	C^{iii}	C^{iv}
Me_2Si22	Li^+	60.72	72.90	58.63	–	–	–	–	−3.40	–	–	–
	Na^+	60.82	73.00	58.63	–	–	–	–	−3.41	–	–	–
	Rb^+	61.04	73.35	58.64	–	–	–	–	−3.43	–	–	–
Me_2Si32	Li^+	60.74	71.58	69.66	71.11	58.58	–	–	−3.49	–	–	–
	Na^+	60.87	71.72	69.74	71.23	58.60	–	–	−3.49	–	–	–
	Rb^+	61.09	71.96	69.89	71.40	58.61	–	–	−3.50	–	–	–
Me_2Si42	Li^+	60.82	71.73	69.51 (2×)		69.69	71.38	58.33	−3.65	–	–	–
	Na^+	60.91	71.84	69.73; 69.64		69.77	71.38	58.31	−3.67	–	–	–
	Rb^+	61.05	71.98	69.91 (2×)		69.86	71.38	58.33	−3.67	–	–	–
EtSi23	Li^+	61.08	72.60	58.42	–	–	–	–	1.70	5.93	–	–
	Na^+	61.11	73.02	58.48	–	–	–	–	1.72	5.94	–	–
	Rb^+	61.44	73.51	58.48	–	–	–	–	1.70	5.94	–	–
EtSi33	Li^+	61.12	71.39	69.66	71.13	58.46	–	–	1.59	5.98	–	–
	Na^+	61.22	71.47	69.76	71.27	58.46	–	–	1.60	5.97	–	–
	Rb^+	61.46	71.60	69.83	71.33	58.47	–	–	1.60	5.98	–	–
EtSi43	Li^+	61.10	71.34	69.64 (2×)		69.70	71.02	58.28	1.49	5.74	–	–
	Na^+	61.23	71.41	69.73; 69.67		69.75	71.14	58.27	1.46	5.73	–	–
	Rb^+	61.31	71.50	69.84 (2×)		69.89	71.25	58.28	1.47	5.75	–	–
PhSi23	Li^+	63.58	74.20	59.69	–	–	–	–	132.68	136.05	129.61	132.65
	Na^+	64.03	74.75	59.86	–	–	–	–	132.87	136.65	129.96	132.87
	Rb^+	64.00	74.91	59.67	–	–	–	–	132.61	136.60	129.77	132.44
PhSi33	Li^+	63.85	72.56	71.65	70.18	59.99	–	–	132.08	136.04	129.71	132.68
	Na^+	64.09	72.47	72.94	70.86	59.93	–	–	130.74	136.52	130.02	133.06
	Rb^+	64.11	72.89	73.11	71.27	59.83	–	–	131.43	136.65	129.90	132.83
PhSi43	Li^+	63.64	72.79	70.24 (2×)		71.58	71.55	59.79	129.92	136.14	129.67	132.65
	Na^+	64.08	73.17	70.75 (2×)		71.03	72.47	60.02	130.92	136.67	130.10	132.87
	Rb^+	64.10	73.22	70.98; 71.03		71.35	72.88	59.93	132.54	136.75	129.78	132.42

TABLE X ^{29}Si Chemical shifts for Si-ligand/cation solutions (R = ratio of [ligand]/[cation])

Complex	^{29}Si chemical shift (ppm) R=2:1	R=1:1	R=1:2
$Me_2Si22+Li^+$	− 42.74	− 42.76	− 42.77
$Me_2Si22+Na^+$	− 42.92	− 42.93	− 42.90
$Me_2Si22+Rb^+$	− 43.09	− 43.12	− 43.11
$Me_2Si32+Li^+$	− 43.96	− 44.01	− 44.04
$Me_2Si32+Na^+$	− 44.10	− 44.17	− 44.14
$Me_2Si32+Rb^+$	− 44.66	− 44.65	− 44.61
$Me_2Si42+Li^+$	− 44.14	− 44.14	− 44.14
$Me_2Si42+Na^+$	− 44.31	− 44.37	− 44.33
$Me_2Si42+Rb^+$	− 44.83	− 44.82	− 44.81
$EtSi23+Li^+$	− 59.92	− 59.67	− 59.67
$EtSi23+Na^+$	− 59.91	− 59.92	− 59.92
$EtSi23+Rb^+$	− 60.11	− 60.02	− 60.04
$EtSi33+Li^+$	− 59.99	− 59.13	− 59.18
$EtSi33+Na^+$	− 60.36	− 59.26	− 59.26
$EtSi33+Rb^+$	− 60.42	− 59.30	− 59.31
$EtSi43+Li^+$	− 60.78	− 59.99	− 60.28
$EtSi43+Na^+$	− 60.72	− 60.06	− 60.31
$EtSi43+Rb^+$	− 60.81	− 60.12	− 60.21
$PhSi23+Li^+$	− 65.22	− 65.13	− 65.13
$PhSi23+Na^+$	− 65.28	− 65.13	− 65.12
$PhSi23+Rb^+$	− 65.29	− 65.15	− 65.16
$PhSi33+Li^+$	− 65.43	− 65.32	− 65.33
$PhSi33+Na^+$	− 65.53	− 65.41	− 65.45
$PhSi33+Rb^+$	− 65.55	− 65.40	− 65.42
$PhSi43+Li^+$	− 65.87	− 65.55	− 65.75
$PhSi43+Na^+$	− 65.85	− 65.49	− 65.58
$PhSi43+Rb^+$	− 65.91	− 65.58	− 65.57

in chemical shifts were observed. The values of these changes depend on the position of the atom in the ligand molecule and the ion in the complex. ^{29}Si NMR chemical shifts of Si-ligand/cation solutions (Table X) showed the formation of only 1:1 complexes for all of the podands studied.

^{7}Li chemical shifts for ligand/lithium ion mixtures and ^{23}Na chemical shifts for ligand/sodium ion mixtures in CD_3CN (293 K) as a function of the ligand/metal molar ratio for Si-podands in CD_3CN (293 K) were measured (Table XI). From these data values of stability constants (log K) for complexes of ligands with Li^+ and Na^+ ions were calculated, and the results are summarized in Table XII. The ESIMS technique was used to determine the stoichiometry of the silicon complexes with lithium and sodium cations, and for all of the podands strong signals of 1:1 complexes with metal ions were observed. The intensity of $(M + Li^+)$ and $(M + Na^+)$ signals obtained in the second ESIMS experiment for the solution of one ligand and excess metal cation mixture (1:1) corresponded to the relation of the stability constants as determined by NMR methods (Fig. 2).

For all of the ligands only a small increase in the values of the stability constants with length of the polyoxaethylene chains in the ligand was observed. The values of the stability constants of the 1:1 complexes for the sodium ions were always higher than for the complexes with lithium

TABLE XI ^{7}Li and ^{23}Na chemical shifts (ppm) for complexes (1:1) of Si podands with lithium(I) and sodium(I) cations in CD_3CN at 293 K

Li^+					^{7}Li NMR				
	$PhSi23+Li^+$	$PhSi33+Li^+$	$PhSi43+Li^+$	$EtSi23+Li^+$	$EtSi33+Li^+$	$EtSi43+Li^+$	$Me_2Si22+Li^+$	$Me_2Si32+Li^+$	$Me_2Si42+Li^+$
− 1.690	− 1.558	− 1.497	− 1.427	− 1.496	− 1.344	− 1.327	− 1.551	− 1.485	− 1.422
Na^+					^{23}Na NMR				
	$PhSi23+Na^+$	$PhSi33+Na^+$	$PhSi43+Na^+$	$EtSi23+Na^+$	$EtSi33+Na^+$	$EtSi43+Na^+$	$Me_2Si22+Na^+$	$Me_2Si32+Na^+$	$Me_2Si42+Na^+$
− 6.351	− 6.243	− 6.209	− 6.204	− 6.191	− 6.144	− 6.150	− 6.275	− 6.243	− 6.237

TABLE XII Stability constants ($\log K$) for the complexes of ligands with Li^+ and Na^+ ions

	Log K	
Ligand	Li^+	Na^+
Me_2Si22	0.6 ± 0.1 (1:1)	0.7 ± 0.1 (1:1)
Me_2Si32	0.8 ± 0.2 (1:1)	1.2 ± 0.2 (1:1)
Me_2Si42	0.9 ± 0.2 (1:1)	1.2 ± 0.1 (1:1)
EtSi23	0.6 ± 0.2 (1:1)	1.9 ± 0.1 (1:1)
EtSi33	1.1 ± 0.1 (1:1)	2.0 ± 0.2 (1:1)
EtSi43	1.2 ± 0.1 (1:1)	2.0 ± 0.1 (1:1)
PhSi23	0.4 ± 0.1 (1:1)	1.3 ± 0.1 (1:1)
PhSi33	0.7 ± 0.1 (1:1)	1.5 ± 0.2 (1:1)
PhSi43	0.9 ± 0.2 (1:1)	1.5 ± 0.3 (1:1)

TABLE XIII Heats of interaction of podands with $SbCl_5$ in CCl_4 solution (1:1 complexes)

Ligand	$-\Delta H$ (kJ mol^{-1})
Me_2Si22	101 ± 8
Me_2Si32	157 ± 12
Me_2Si42	204 ± 14
EtSi23	210 ± 13
EtSi33	315 ± 22
EtSi43	424 ± 23
PhSi23	181 ± 6*
PhSi33	268 ± 15*
PhSi43	356 ± 16*

*Ref. [8].

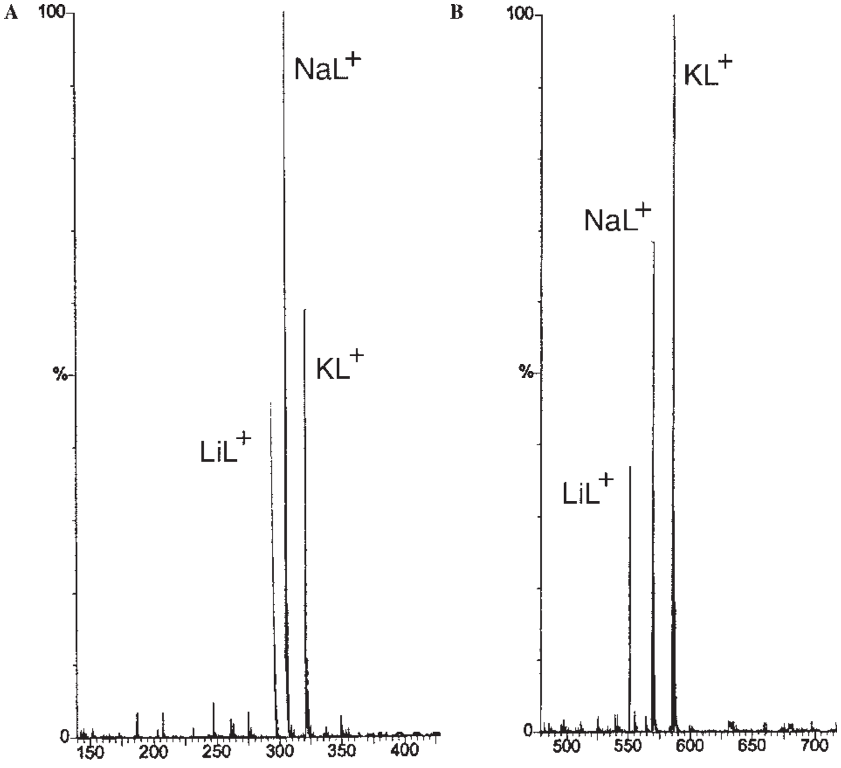


FIGURE 2 Intensity of $(M + Li^+)$, $(M + Na^+)$ and $(M + K^+)$ signals obtained in ESIMS experiment for the solution of EtSi23 (a) and EtSi43 ligands (b) with excess metal cation ($Li^+ : Na^+ : K^+$) mixture (1:1:1).

ions. The silicon ligands formed 1:1 complexes with $SbCl_5$ in different solvents. Heats of reaction were determined using calorimetric titration of the podand compounds with $SbCl_5$, both dissolved in CCl_4. These values depended strongly on the length of the polyoxaethylene chains in the ligand molecules and increased with the number of oxygen atoms in the podand (Table XIII).

The results show that the addition of cations to podand solvents or $SbCl_5$ molecules give 1:1 complexes. As a result of the self-organization process, ion or molecular channels were formed. These podands could be used as strong complexation solvents for organic reactions when the reagents are salts or molecules with electron acceptor atoms.

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