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Potentiometric and AM1d studies of silicon podands—silver(I) complexes

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Abstract

Formation of complexes of various silicon podands and silver(I) cations in propylene carbonate has been studied by the potentiometric and AM1d semiempirical methods. Silicon podands form stable complexes with Ag^+ cations. The stability constants of various complexes are determined. It has been shown that the number of Ag^+ cations complexed by the Si-podands depends strongly on the number of oxygen atoms in the oxaalkyl chains. The PhSi15.3 podand can complex as many as 6 silver(I) cations. The structures of these complexes are visualised by the AM1d semiempirical method.

Keywords: Supramolecular chemistry; Ionic channels; Potentiometric method; Si-podand; Silver(I) complexes; AM1d calculations; Stability constant

1. Introduction

The macrocyclic compounds form with some metal cations complexes of different stoichiometry [1,2]. Podands are acyclic compounds characterised by a similar capability of complex formation with metal ions as crown ethers and cryptands [3]. In earlier papers we have studied the complexes of various inorganic esters of ethylene glycols and their derivatives with monovalent cations such as Li^+, Na^+ or K^+ [4–13] using multinuclear NMR, FT-IR and calorimetric methods. In these papers we have demonstrated that the compounds including two or three oxaalkyl chains bonded with phosphorus, boron, sulphur or silica atoms, have formed complexes with the cations mentioned. Within the complexes the cations have shown easy cation polarisability due to their very fast fluctuations between the oxygen atoms of the chains [4,5,14].

Crown ethers can form with silver(I) cations complexes of 1:1, 2:1, 3:2 and 2:3 stoichiometry in solution [15]. Similarly to crown ethers also podands with silver(I) form complexes and this process has been studied by the potentiometric and AM1d methods.

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2. Experimental

The silicon podands were synthesised according to the method described in papers [3,4]. MA and Si2.4Bu ligands were used as commercial products. Propylene carbonate used as a solvent for potentiometric studies was from Merck.

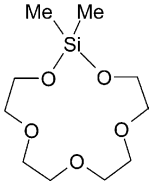
2.1. Potentiometric measurements

The potentiometric method used was described in Ref. [16]. The potentiometric titration was performed in propylene carbonate at 25 °C using an OP-205 Radelkis pH-meter linked to a personal computer via a PCL-838 control card. The equilibrium constants were calculated using the program STOICHIO based on the non-linear least-squares Gauss–Newton–Marquardt algorithm [17].

2.2. AM1d semiempirical calculations

AM1d semiempirical calculations were performed using the Win Mopac 2003 program [18,19]. Full geometry optimisation of the studied complexes of Si-podand with silver(I) cations was carried out without any symmetry constraints [20].

Table 1
The formulae of the Si-podands and their abbreviations

Podands	Abbreviation name
$Me_2Si(OCH_2CH_2OCH_3)_2$	$Me_2Si2.2$
$Me_2Si[(OCH_2CH_2)_2OCH_3]2$	$Me_2Si3.2$
$Me_2Si[(OCH_2CH_2)_3OCH_3]2$	$Me_2Si4.2$
$EtSi(OCH_3)_3$	EtSi1.3
$EtSi(OCH_2CH_2OCH_3)_3$	EtSi2.3
EtSi $[(OCH_2CH_2)_2OCH_3]_3$	EtSi3.3
EtSi $[(OCH_2CH_2)_3OCH_3]_3$	EtSi4.3
$PhSi(OCH_2CH_2OCH_3)_3$	PhSi2.3
$PhSi[(OCH_2CH_2)_7OCH_3]_3$	PhSi7.3
$PhSi[(OCH_2CH_2)_{12}OCH_3]_3$	PhSi13.3
$PhSi[(OCH_2CH_2)_{14}OCH_3]_3$	PhSi15.3
$PhSi[O(CH_2)_7CH_3]_3$	$PhSi1_{alkil}3$
$Si(OCH_2CH_2OBu)_4$	Si2.4Bu
	MA
$Me_3Si(OCH_2CH_2)_4OC_{12}H_{25}$	$Me_3Si5.1D$
$Me_2Si[(OCH_2CH_2)_4OC_{12}H_{25}]_3$	$Me_2Si5.2D$
$PhSi[(OCH_2CH_2)_4OC_{12}H_{25}]_3$	PhSi5.3D
$EtSi[(OCH_2CH_2)_4OC_{12}H_{25}]_3$	EtSi5.3D
$PhSi[(OCH_2CH_2)_2OC_{16}H_{33}]_3$	PhSi3.3H
$EtSi[(OCH_2CH_2)_2OC_{16}H_{33}]_3$	EtSi3.3H
$[C_{12}H_{25}O(CH_2CH_2O)_4]_3SiCH_2CH_2Si[(OCH_2CH_2)_4OC_{12}H_{25}]_3$	$D3.5SiCH_2CH_2Si5.3D$

3. Results and discussion

The formulae and their abbreviations for the studied podands are shown in Table 1.

3.1. Potentiometric measurements

An exemplary potentiometric titration curve of Ag(I) with silicon podands in propylene carbonate is shown in Fig. 1. All the curves obtained exhibited characteristic features indicating the coexistence of different complexes. The stability constants (K_i) of i:1 silver(I):podand complexes were calculated for the following equilibria:

$$(Ag_{(i-1)}L)^{(i-1)+} + Ag \overset{K_i}{\rightleftharpoons} (Ag_iL)^{i+}$$

where $i = 1, 2, 3\ldots$ and for 1:2 complexes of silver(I):podand the stability constants K_{2L} were calculated for the equilibrium:

$$(AgL^+ + L \overset{K_{2L}}{\rightleftharpoons} (AgL_2)^+$$

The stability constants of silver(I) complexes with podands in propylene carbonate at 25 °C are collected in Table 2. The data given in Table 2 indicate the formation of two types of complexes in propylene carbonate as solvent, i.e. Ag_iL^{i+} (log K_i) and AgL_2^+ (log K_{2L}). It is interesting to note that with increasing number of the oxygen atoms in the chains the formation of the Ag_iL^{i+} complexes is favoured. The number of the oxygen atoms in the chains also determines the stoichiometry of the complexes, i.e. their structure.

In all cases the most favourable structure of the complex formed between silver(I) and Si-podand is the complex of 1:1 stoichiometry. With increasing numbers of the oxygen atoms in the chains the value of stability constants of these complexes strongly increases. For instance the highest value of the stability constant for the 1:1 complex with silver(I) is observed for PhSi15.3 ligand for which log $K_1 = 6.01$. At the same time the stability constants for complexes with other stoichiometries decrease with increasing number of the complexed silver(I) cations. This is especially pronounced for the Si-podand with large oxyalkyl chains such as PhSi7.3, PhSi13.3, PhSi15.3 and $D3.5SiCH_2CH_2Si5.3D$ (Table 2).

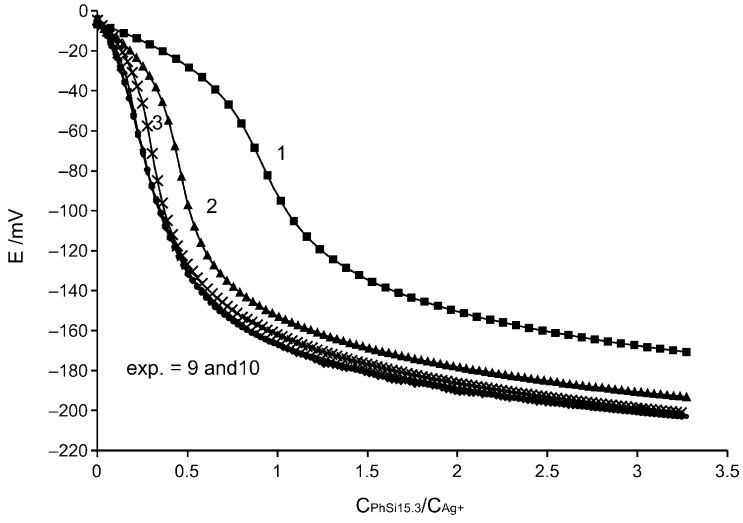


Fig. 1. The potentiometric measurement of silver(I) perchlorate (6.00×10^{-3} mol dm^{-3}) with PhSi15.3 podand as a function of the molar ratio $C_{PhSi15.3}/C^+_{Ag}$. The experimental points are (*) and results of the fit by the models: 1 (■), 2 (△), 3 (×), 9 (○), 10(●).