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Potentiometric and AM1d studies of a new class of Tr-podands–silver(I) complexes

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Formation of complexes of structurally comparable six silicon, boron and phosphorous Triton X podands (Tr-podands) and silver(I) cations in propylene carbonate has been studied by the potentiometric and AM1d semi-empirical methods. Three types of these podands (**2**–**7**) form stable complexes with Ag^+ cations. The stability constants of the complexes including different number of silver(I) cations are determined. It has been shown that the number of Ag^+ cations complexed by the podands depends strongly on the number of oxaalkyl chains and on the type of central podand's atom (Si, B or P). The (**7**) podand (with six polyoxaalkyl chains) can complex as many as six silver(I) cations. The structures of these complexes are visualised by the AM1d semi-empirical method.

Keywords: supramolecular chemistry; potentiometric method; Tr-podand; silver(I) complexes; AM1d calculations; stability constant

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1. Introduction

The macrocyclic compounds, both cyclic and acyclic, are able to form complexes of different stoichiometry with some metal cations (*1–4*). Podands are acyclic compounds characterised by a similar capability of complex formation with metal ions as crown ethers and cryptands (*5*, *6*). 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^+ using multinuclear NMR, FT-IR, calorimetric, potentiometric and semi-empirical (PM3, PM5) methods (*7–12*). We have also shown (*13–15*) that the silicon and phosphorus podands form stable complexes with silver(I) cations of various stoichiometry depending on the length of the oxaalkyl chains.

Triton X surfactants are used in numerous commercial and industrial products. Large amounts of such surfactants and their various residual biodegradation by-products are ultimately released into the environment. We have recently published a paper reporting the first synthesis of a group of Tr-polypodands (Triton X polypodands) with different central atoms, such as Si, B or P. Results of this study demonstrate the application of these new compounds in some organic reactions in the phase transfer catalysis conditions (*16*).

In this paper, we want to demonstrate the results of a study of complex formation between Triton X (**1**) and new six Tr-podands (**2**–**7**) (Figure 1) including two or three oxaalkyl chains bonded with phosphorus, boron, sulphur or silica atoms or six polyoxaalkyl chains (**7**) and silver(I) cations and as well as their structures. This process has been studied by the potentiometric and AM1d methods.

2. Experimental

The Tr-podands (**2**–**7**) were synthesised according to the method described in the papers (*16*). Triton X-100 was a commercial product (Aldrich). Propylene carbonate used as a solvent for potentiometric studies was from Merck.

2.1 Potentiometric measurements

The potentiometric method used was described in Ref. (*17*). 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 nonlinear least-squares Gauss–Newton–Marquardt algorithm (*18*).

2.2 AM1d semi-empirical calculations

AM1d semi-empirical calculations were performed using the Win Mopac 2003 program. Full geometry optimisation of the studied complexes of Si-podand with silver(I) cations was carried out without any symmetry constraints (*19*).

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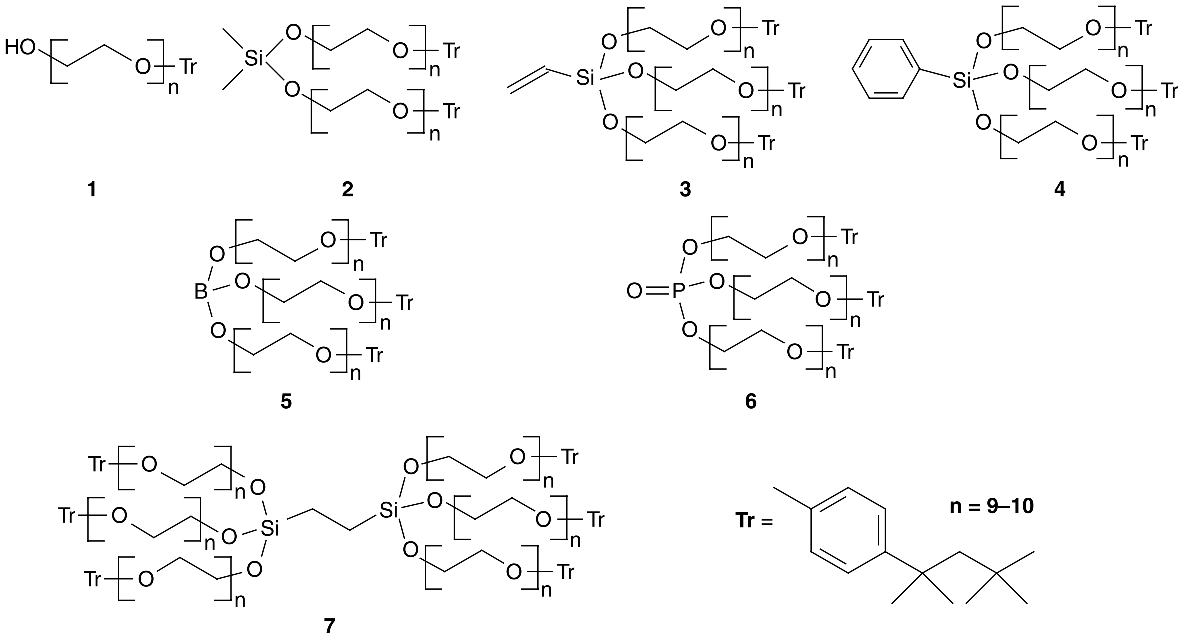

Figure 1. Compounds studied.

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3. Results and discussion

The formulae of the podands studied and their abbreviations are shown in Figure 1.

3.1 Potentiometric measurements

The stability constants (K_i) of i:1 silver(I):Tr-podand complexes were calculated for the following equilibria Equations (1) and (2):

$$\left(\mathrm{Ag}_{(i-l)}\mathrm{L}\right)^{(i-l)+} + \mathrm{Ag}^{+} \overset{K_i}{\rightleftharpoons} \left(\mathrm{Ag}_i\mathrm{L}\right)^{i+}, \qquad (1)$$

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

$$\mathrm{AgL}^{+} + \mathrm{L} \overset{K_{2\mathrm{L}}}{\rightleftharpoons} \left(\mathrm{AgL}_2\right)^{+}. \qquad (2)$$

The stability constants of silver(I) complexes with Triton X podands in propylene carbonate at 25°C are collected in Table 1. The data given in Table 1 indicate the formation of two types of complexes in propylene carbonate as solvent, i.e. $\mathrm{Ag}_i\mathrm{L}^{i+}$ ($\log K_i$) and AgL_2^+ ($\log K_{2\mathrm{L}}$).

We observed that with increasing number of the polyoxaalkyl chains and the same number of oxygen atoms in the molecule, the formation of the $\mathrm{Ag}_i\mathrm{L}^{i+}$ complexes is favoured. This fact also determines the stoichiometry of the complexes, i.e. their structures. In all cases, the most favourable structure of the complex made by silver(I) and Si-podand is the 1:1 stoichiometry. For the complexes of podands **1**–**6**, the type of the Tr-podand's central atom does not influence the value of the stability constants of these complexes. The constants of complexation of silver with podand 7 containing six polyoxaethylene chains are slightly higher than those of the complexes of the same stoichiometry but with different podands. For instance, the highest value of the stability constant for the 1:1 complex with silver(I) for ligand **7** is $\log K_1 = 6.89 \pm 0.06$. The stability constants of the complexes with other

Table 1. The stability constants ($\log K_i$) and ($\log K_{2\mathrm{L}}$) of the complexes of Tr-podands with silver(I) cations in propylene carbonate at 25°C.

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$	$\log K_{2\mathrm{L}}$
1	5.46 ± 0.03	4.22 ± 0.05	–	–	–	–	–
2	6.12 ± 0.05	5.16 ± 0.09	4.63 ± 0.12	–	–	–	3.26 ± 0.17
3	6.03 ± 0.05	5.66 ± 0.08	4.94 ± 0.10	4.62 ± 0.11	–	–	3.55 ± 0.18
4	5.94 ± 0.03	5.45 ± 0.05	4.91 ± 0.09	4.29 ± 0.12	–	–	–
5	5.73 ± 0.04	5.48 ± 0.07	4.86 ± 0.10	4.45 ± 0.13	–	–	0.98 ± 0.26
6	6.09 ± 0.05	5.61 ± 0.08	4.48 ± 0.11	4.11 ± 0.14	–	–	3.95 ± 0.20
7	6.89 ± 0.06	6.14 ± 0.14	5.53 ± 0.10	5.15 ± 0.18	4.95 ± 0.13	4.35 ± 0.26	–

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Table 2. The heat of formation (HOF) of podands and their energetically favourable complexes with Ag$^+$ cations.

No. of compounds	Compound	Mixture	HOF (kJ/mol)	ΔHOF (kJ/mol)
1	Triton	Tr	−2144.21	
		Tr:Ag$^{+}_{\text{(uncomplexed)}}$	−1128.70	−407.01
		Tr:Ag$^{+}_{\text{(complexed)}}$	−1535.71	
		Tr:2Ag$^{+}_{\text{(uncomplexed)}}$	−113.19	−655.11
		Tr:2Ag$^{+}_{\text{(complexed)}}$	−768.30	
		Tr:3Ag$^{+}_{\text{(uncomplexed)}}$	902.32	−516.27
		Tr:3Ag$^{+}_{\text{(complexed)}}$	386.05	
2	Si2Me	Si2Me	−4517.90	
		Si2Me:2Ag$^{+}_{\text{(uncomplexed)}}$	−2486.88	−788.07
		Si2Me:2Ag$^{+}_{\text{(complexed)}}$	−3274.95	
		Si2Me:3Ag$^{+}_{\text{(uncomplexed)}}$	−1471.37	−806.06
		Si2Me:3Ag$^{+}_{\text{(complexed)}}$	−2277.43	
		Si2Me:4Ag$^{+}_{\text{(uncomplexed)}}$	−455.86	−749.20
		Si2Me:4Ag$^{+}_{\text{(complexed)}}$	−1205.06	
3	SiVin	SiVin	−6593.82	
		SiVin:2Ag$^{+}_{\text{(uncomplexed)}}$	−4562.80	−722.43
		SiVin:2Ag$^{+}_{\text{(complexed)}}$	−5285.23	
		SiVin:3Ag$^{+}_{\text{(uncomplexed)}}$	−3547.29	−906.00
		SiVin:3Ag$^{+}_{\text{(complexed)}}$	−4453.29	
		SiVin:4Ag$^{+}_{\text{(uncomplexed)}}$	−2531.78	−1032.21
		SiVin:4Ag$^{+}_{\text{(complexed)}}$	−3563.99	
		SiVin:5Ag$^{+}_{\text{(uncomplexed)}}$	−1516.27	−947.54
		SiVin:5Ag$^{+}_{\text{(complexed)}}$	−2463.81	
4	SiPh	SiPh	−6553.02	
		SiPh:2Ag$^{+}_{\text{(uncomplexed)}}$	−4522.00	−736.49
		SiPh:2Ag$^{+}_{\text{(complexed)}}$	−5258.49	
		SiPh:3Ag$^{+}_{\text{(uncomplexed)}}$	−3506.49	−934.72
		SiPh:3Ag$^{+}_{\text{(complexed)}}$	−4441.21	
		SiPh:4Ag$^{+}_{\text{(uncomplexed)}}$	−2490.98	−1043.85
		SiPh:4Ag$^{+}_{\text{(complexed)}}$	−3534.83	
		SiPh:5Ag$^{+}_{\text{(uncomplexed)}}$	−1475.47	−854.62
		SiPh:5Ag$^{+}_{\text{(complexed)}}$	−2330.09	
5	B	B3	−6630.45	
		B3:2Ag$^{+}_{\text{(uncomplexed)}}$	−4599.43	−718.82
		B3:2Ag$^{+}_{\text{(complexed)}}$	−5318.25	
		B3:3Ag$^{+}_{\text{(uncomplexed)}}$	−3583.92	−908.84
		B3:3Ag$^{+}_{\text{(complexed)}}$	−4492.76	
		B3:4Ag$^{+}_{\text{(uncomplexed)}}$	−2568.41	−1011.89
		B3:4Ag$^{+}_{\text{(complexed)}}$	−3580.30	
		B3:5Ag$^{+}_{\text{(uncomplexed)}}$	−1552.90	−802.11
		B3:5Ag$^{+}_{\text{(complexed)}}$	−2355.01	
6	PO	PO	−6852.14	
		PO:2Ag$^{+}_{\text{(uncomplexed)}}$	−4821.12	−671.84
		PO:2Ag$^{+}_{\text{(complexed)}}$	−5492.96	
		PO:3Ag$^{+}_{\text{(uncomplexed)}}$	−3805.61	−868.51
		PO:3Ag$^{+}_{\text{(complexed)}}$	−4674.12	
		PO:4Ag$^{+}_{\text{(uncomplexed)}}$	−2790.10	−967.52
		PO:4Ag$^{+}_{\text{(complexed)}}$	−3757.62	
		PO:5Ag$^{+}_{\text{(uncomplexed)}}$	−1774.59	−884.20
		PO:5Ag$^{+}_{\text{(complexed)}}$	−2658.79	
7	Si2	2Si2	−13,372.70	
		Si2:4Ag$^{+}_{\text{(uncomplexed)}}$	−9310.68	−1340.55
		Si2:4Ag$^{+}_{\text{(complexed)}}$	−10,651.20	
		Si2:6Ag$^{+}_{\text{(uncomplexed)}}$	−7279.66	−1580.96
		Si2:6Ag$^{+}_{\text{(complexed)}}$	−8860.62	
		Si2:8Ag$^{+}_{\text{(uncomplexed)}}$	−5248.64	−1217.30
		Si2:8Ag$^{+}_{\text{(complexed)}}$	−6465.94	

$\Delta\text{HOF} = \text{HOF}_{\text{(complexed)}} - \text{HOF}_{\text{(uncomplexed)}}$.

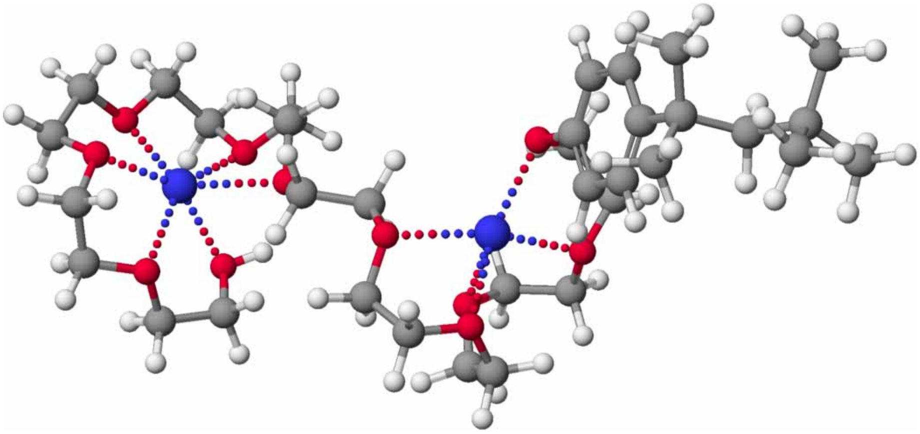

Figure 2. Calculated structure of triton (**1**) with two Ag^+ cations.

stoichiometries decrease with increasing number of the complexed silver(I) cations (Table 1).

3.2 AM1d semi-empirical calculations

The values of HOF of the complexes of triton and triton-based podands and different numbers of silver(I) cations are collected in Table 2. These data show that the HOF of the complex strongly depends on the number of silver cations complexed. The ΔHOF is the difference between the HOF of the complex and the sum of HOFs of the isolated ligand and cations. For Triton (**1**), addition of up to two silver cations decreases the value of ΔHOF, addition of another cation increases this value, making the complex unstable. This means that, for this complex, the stoichiometry of 1ligand:2Ag^+ is preferred. For the podands studied other stoichiometries are possible, the number of the complexed cations vary and strongly depend on the number of oxygen atoms in the host molecule. For podand (**2**) the preferred stoichiometry is 1:3, for podand (**7**) it is 1:6 and for all other podands (**3**–**6**) it is 1:4. The podands with tri-pendant arms have the same number of oxygen atoms and differ only in the type of the central atom or when the central atom is Si, in the extra group on this atom. These differences for triton podands have only slight effect on its complexation ability, the ΔHOFs change only by a few percent. This correlates well with the potentiometric data. In our previous study (*15*) with podands ending with alkyl groups, the influence of the central atom was greater. We suggest that 'marginalisation of central atom' is the effect of the bulk ending of the triton chain. The visualisation of the energetically favourable structures of triton (**1**) with two Ag^+ cations and podand (**4**) with four Ag^+ cations are shown in Figures 2 and 3, respectively. In Figure 3, in addition, the 'bulk' effect of the triton ending group is shown.

It is interesting to note that the formation of complexes of the 2:1 stoichiometry is indicated by the log K_{2L} values. The value of this constant for complex (**5**) is significantly smaller (log $K_{2L} = 0.98$) than the corresponding values of the other Tr-podand complexes (2L) (log K_{2L} of about 4.0). According to these values, the formation of complexes of compound (**5**) with B as the central atom with silver is less favourable than that of the same type of complexes with Si-ligands (compounds: **3** or **4**). The same tendency is observed for the HOF of these complexes, calculated by AM1d. For the 2:1 complex of compound (**5**), the complex formation energy is about -444.07 kJ, but for compound (**3**) it is about -579.38 kJ. The difference follows from the structures of these complexes. In the process of formation

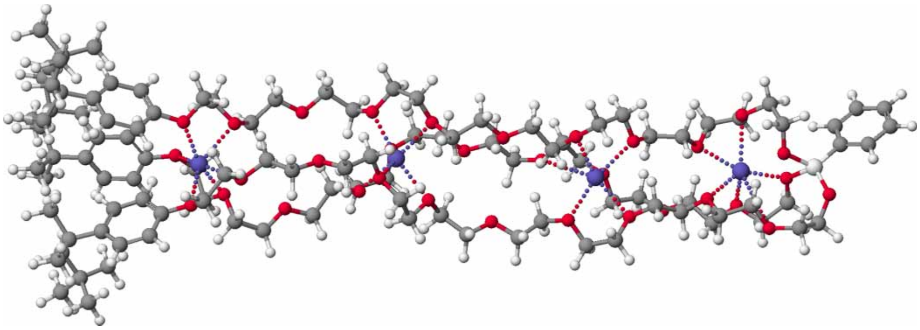

Figure 3. Calculated structure of podand (**4**) with four Ag^+ cations.

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of the complex composed of two ligand 5 and one silver ion, one chain from each ligand is involved, while the other chains are not engaged in the complexation. In the process of formation of the complex of two ligands with Si as the central atom and one silver cation, two chains from each ligand are involved.

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