Hybrid organic–inorganic materials. Preparation and properties of dibenzo-18-crown-6 ether-bridged polysilsesquioxanes

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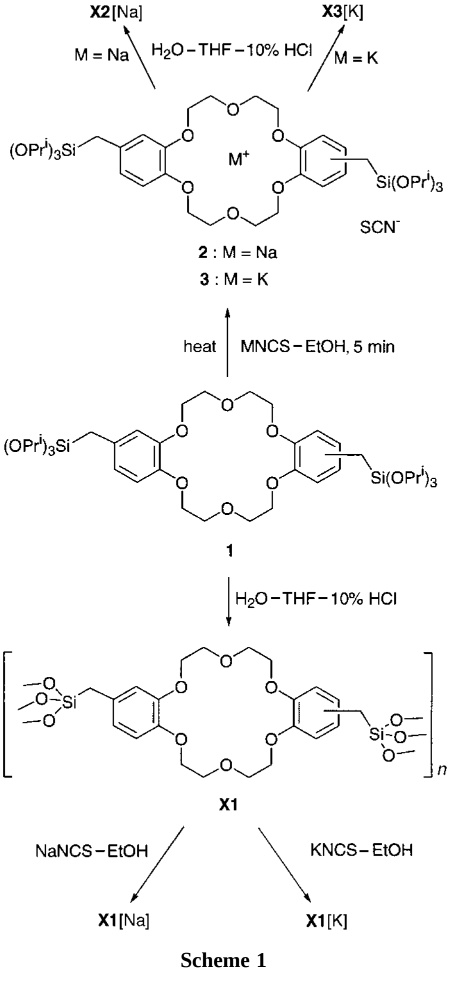
The complexation of alkali metal cations (Na$^+$ and/or K$^+$) by organic–inorganic hybrid materials incorporating dibenzo-18-crown-6 ether moieties covalently linked to silica by two Si–C bonds is explained in terms of deformations of the crown ether moiety during the sol–gel process

Crown ethers[1] immobilised on organic or inorganic polymers,[2] have been widely used for the separation of alkali or alkaline earth metal ions. The use of silica as an inorganic polymer is interesting especially for ion chromatography[2] and as an ion transport membrane.[3,4] Crown ethers can be linked to the stationary phase either dynamically[5] (physically absorbed) or through a covalent bond. Up to now two methods have been used to chemically bond the crown ether to the silica framework. The first consists of anchoring either a crown ether to a chemically modified silica[6] or a silylated crown ether to silica.[7,8] The second method is the co-hydrolysis and co-polymerisation of a mixture of a crown ether bearing one hydrolysable Si(OR)$_3$ group with a tetraalkoxysilane[9] or an organotriethoxysilane[9–11] by using the sol–gel process.[12] In both cases, the crown ether is co-valently bound to the matrix by only one Si–C bond and it is located at the surface.[13,14] Recently, the sol–gel process has been used to prepare hybrid organic–inorganic materials by hydrolysis and polycondensation of organic molecules substituted by more than one hydrolysable Si(OR)$_3$ group.[15–17] It has been shown that in this case the organic units can be incorporated into the silica matrix. Furthermore, a short-range organisation has been found by means of chemical reactivity studies.[16,17]

We report here the preparation of the 4,4′(5′) mixture of the bisilylated 18-crown-6-ethers **1**, as well as its hydrolysis and polycondensation by the sol–gel process and the study of the binding ability of the resulting solid towards Na$^+$ and/or K$^+$.

Bisilylated crown ether **1** was prepared by reaction of triisopropyloxysilylmethylmagnesium chloride[18] with the commercial mixture of 4,4′(5′)-dibromo-18-crown-6.† Treatment of **1** with 1 equiv. of NaSCN or KSCN in EtOH gave the corresponding complexes **2** and **3** respectively in high yield (Scheme 1). Sol–gel polycondensation of **1**, **2** and **3** was performed at room temperature in THF solution (1 M for **1** and 0.5 M for **2** and **3**) in the presence of a stoichiometric amount of water (3 equiv.) and 10% of HCl as catalyst. The gel formation is very fast (< 5 min) for **2** and **3** but takes nearly 12 h for **1**. This large difference in gel times could be attributed to an increased rigidity for **2** and **3** compared to that of **1** and most probably to a partial protonation of the free oxygen atoms of the crown ether **1**, thus decreasing the catalytic activity of HCl. The gels were allowed to age for five days at room temperature and were powdered and washed twice with ethanol followed by diethyl ether and dried at 120 °C under vacuum (20 mm Hg) for 12 h. From ^{29}Si CP MAS NMR spectroscopy it was shown that the xerogels **X1**, **X2**[Na] and **X3**[K} all display one major resonance centred at δ −62 (substructure T^2 [C–Si(OR)(OSi)$_2$]). Thus, in spite of different gel times the degrees of polycondensation lie in the same range. The specific surface areas of these three xerogels, determined by adsorption–desorption of N$_2$ (BET), were found to be very low (< 10 m^2 g^{-1}). Furthermore, during the sol–gel polymerisation of **2** and **3**, 95% of Na$^+$ cations and 96% of K$^+$ cations were retained within the xerogel (as measured by elemental analysis) which indicates that the conformation of the crown-ether moiety was not distorted during the sol–gel process.

The xerogel **X1** was treated with 1 equiv. of NaSCN or KSCN in EtOH for 12 h at room temperature or under reflux. The amount of non-complexed cations was measured by flame spectrophotometry after filtration of the solid followed by washing with EtOH until no more salt was recovered, and then evaporation of the solvent, and solubilisation of the remaining alkali metal salt in water. From these data the amount of cations incorporated into **X1** was inferred (Table 1). Further confirmation of the complexation of Na$^+$ and K$^+$ cations into **X1** was given by IR spectroscopy (DRIFT). Indeed, $\nu(C\equiv N)$ frequencies of NaSCN and KSCN incorporated into **X1** appear respectively



Scheme 1

Table 1 Yield (%) of alkali metal cations incorporated into xerogel **X1**

Salt	T/°C	%Na^+	%K^+
NaSCN	20	47^a, 47^b	
	78	43^a, 46^b	
KSCN	20		72^b, 73^b
	78	12^b	72^a, 76^b
NaSCN–KSCN (1 : 1)[c]	78	10^b	74^a, 76^b

[a] Measured by flame spectrophotometry. [b] Measured by microanalysis. [c] Competitive experiments.

at 2068 and 2059 cm^{-1} (2073 and 2024 cm^{-1} for NaSCN and at 2042 and 2004 cm^{-1} for KSCN). The formation of the Na^+ complex was also shown by solid state ^{23}Na NMR spectroscopy. The ^{23}Na NMR spectrum of **X1**[Na] displays one broad signal centred at δ −25 (δ −10.6 for NaSCN under the same conditions). The poor yield (43–47%) of complexation of Na^+ cations into **X1** could be due to the rigidity of the crown ether moiety bound to the inorganic matrix, rigidity which did not allow the crown ether to adopt the more favorable conformation for the Na^+ complexation.

Competition experiments from a 1 : 1 mixture of NaSCN and KSCN in EtOH were likewise investigated using the same method of titration by flame spectrophotometry (Table 1). About 10% of the crown-ether moieties are able to complex Na^+ in the presence of K^+. As about 45% of the crown-ether moieties are able to complex Na^+ in the absence of K^+, we can conclude that about 35% of the complexing sites are able to complex both ions but should be more specific for K^+. If we compare the results of the competition experiments with those for the complexation of K^+, we can infer that about 40% (75 − 35) of the crown ether moieties are specific for K^+. Thus from the overall results it appears that the crown-ether sites are of three types: (1) specific for Na^+ (*ca.* 10%), (2) able to complex both ions but more specifically K^+ (*ca.* 35%) and (3) specific for K^+ (*ca.* 40%). One explanation could be that during the sol–gel process the crown ether undergoes steric constraints which distort the rings giving rise, in the xerogel, to sites which are specific for the complexation of Na^+ and/or K^+. Furthermore from the competition experiments, it appears that 85–90% of the crown ether moieties are accessible to the salts, though the crown-ether moieties are most probably located in the core of the solid in contrast to the case of crown-ether grafted to silica.[6–8] In order to analyse the surface composition of these materials, TOF-SIMS investigations[14] are currently in progress.

Notes and references

† *Experimental procedure*. A mixture of 80.4 ml (579 mmol) of a THF solution of $(Pr^iO)_3SiCH_2MgCl$,[18] 10 g (19.2 mmol) of 4,4′(5′)-dibromo-18-crown-6, and 630 mg (1.16 mmol) of $(PPh_3)_2NiCl_2$ in THF (200 ml) was heated under reflux for 48 h. The THF was removed under vacuum and 150 ml of ether was added to precipitate the salts. After filtration and removal of ether under vacuum, 35.4 g of the $MgCl_2$–crown ether complex was obtained as a brown oil. Decomplexation was accomplished by heating the complex in 200 ml of MeOH under reflux overnight. MeOH was removed under vacuum and 150 ml of pentane was added. A precipitate was formed which was filtered and washed with pentane (3 × 50 ml). Evaporation of pentane gave 17.6 g of a yellow oil which was purified by chromatography to give 6 g (7.52 mmol, 39%) of **1** as a white oil.

NMR ($CDCl_3$): ^1H, δ 1.07 (d, 36H, d, CH_3), 2.02 (s, 4H, CH_2Si), 3.93 (m, 8H CH_2O), 4.07 (m, 14H, CH_2O + CH), 6.66–7.02 (m, 6H, aryl); ^{13}C, δ 21.15 (CH_2Si), 25.9 (CH_3), 65.6 (CH), 69.2, 69.7, 70.45, 70.52, 70.63 (CH_2O), 114.55, 114.67, 115.38, 115.49, 121.96 (CH aryl), 131.8, 146.4, 148.96 (C aryl); ^{29}Si, δ −54.8. Satisfactory elemental analyses (C, H, Si) were obtained.

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