Organic–inorganic hybrid materials. Preparation and properties of dibenzo-18-crown-6 ether-bridged polysilsesquioxanes†

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Dibenzo-18-crown-6 ether derivatives bearing two (**1**, **2**) or four (**3**) hydrolysable Si(OR)$_3$ groups have been synthesised. Their hydrolysis and polycondensation gave rise to new hybrid organic–inorganic materials incorporating dibenzo-18-crown-6 ether moieties covalently linked to silica by two or four Si–C bonds. The complexation of alkali metal cations (Na$^+$ and/or K$^+$) by these materials was investigated. A survey of the uptake of cations showed that four types of chelating sites exist within these materials, the ratio of which depends on the nature of the precursor (flexibility of the spacers between the benzene rings and the silicon centres and number of hydrolysable Si(OR)$_3$ groups) and also on the degree of condensation σ of the polysiloxane network. Furthermore, the complexation of K$^+$ by the precursors **1**, **2** and **3** and of Na$^+$ by **1** were performed quantitatively. During the sol–gel polymerisation of these complexes it was shown that about 95% of the alkali cations were retained within the xerogel. This study proves that the two routes of incorporation of salts within these hybrid materials are not equivalent.

Introduction

The preparation of materials able to strongly complex metal cations is of great interest[1,2] as much from a fundamental point of view (study of their reactivity and coordination chemistry within the solid), as for the wide possibilities that open for physical properties. They offer also potential applications to perform selective metal cation separations. The strong and selective interactions of crown ethers with specific alkali and alkaline earth metal ions make these ligands ideal candidates for such uses.[2,3] Therefore their immobilization on organic or inorganic polymers has been widely studied.[4] In order to avoid the gradual loss of the expensive ligand and the subsequent decrease of the extraction effectiveness the covalent attachment of the macrocyclic ligand to a solid support is required. For this purpose, the binding of crown ethers to silica gel *via* pendant SiOH groups has often been reported.[5–10] However, this method of attachment presents some drawbacks especially as the content of organic moieties is often low and uncontrolled and the dispersion in the final materials is random.

Another method used to covalently attach a crown ether to silica is the co-hydrolysis and co-polymerisation of a mixture of a crown ether bearing one hydrolysable Si(OR)$_3$ group with a tetraalkoxysilane or an organotriethoxysilane[11,12] by using the sol–gel process.[13] In this way, the concentration of chelating groups in the solids is controlled but the dispersion of organic moieties remains random.

Our interest in the study of organic–inorganic hybrid materials[14–16] led us to study the properties of solids obtained by hydrolysis and polycondensation of crown ethers substituted by more than one hydrolysable Si(OR)$_3$ group.

We have prepared as precursors the bissilylated dibenzo-18-crown-6 ethers **1** and **2** and the tetrasilylated dibenzo-18-crown-6 ether **3**, the binding ability of the dibenzo-18-crown-6 ether being well known.[17] **1** presents a methylene group as spacer between the benzene rings and two hydrolysable Si(OiPr)$_3$ groups while **2** and **3** present rigid spacers (ethenyl

group), the monomer **2** having two hydrolysable Si(OEt)$_3$ groups and the precursor **3** four hydrolysable Si(OMe)$_3$ groups. The hydrolysis and polycondensation of these monomers by using the sol–gel process are reported in this paper. It is worth noting that membranes incorporating dibenzo-18-crown 6-ether moieties have been prepared by the sol–gel process to facilitate the competitive transport of silver/copper ions.[18] Our purpose was different. While it was shown that macrocycles such as 15-crown-5 ether and 18-crown-6 ether grafted to silica have approximately the same affinity for metal cations as the corresponding unbound macrocycles in aqueous solutions,[6,8] it seemed to us interesting to investigate the binding ability of dibenzo-18-crown-6 ether moieties incorporated within materials prepared by the sol–gel process towards Na$^+$ and/or K$^+$ ions in relation with the characteristics of the precursor: number of hydrolysable Si(OR)$_3$ groups, nature of the spacer and degree of condensation of the network. It results from this study that the rules of complexation within hybrid organic–inorganic materials are different from those existing in solution.

Results

Bissilylated crown ether **1**[19] was obtained by nickel-catalysed cross-coupling reaction[20] between triisopropyloxysilylmethyl-magnesium chloride[21] and the commercially available mixture of 4,4′(5′)-dibromodibenzo-18-crown-6 ether (Scheme 1). Bissilylated precursor **2** was prepared by Pd-catalysed cross-coupling reaction of the mixture of 4,4′(5′)-dibromodibenzo-18-crown-6 ether with vinyltriethoxysilane (modified Heck reaction[22]) in 58% yield (Scheme 1). Tetrasilylated precursor **3** was prepared in the same way as **2** from the tetrabromodibenzo-18-crown-6 ether. The preparation of this last one by bromination of dibenzo-18-crown-6 ether[23] in CHCl$_3$ provided the tetrabromodibenzo-18-crown-6–hydrogen tribromide complex[24] as a side product in addition to the expected product. In order to avoid this side reaction, acetic acid was used as solvent to yield the expected tetrabromodibenzo-18-crown-6 ether in 80% yield. **3** was isolated in 35% yield as a very moisture
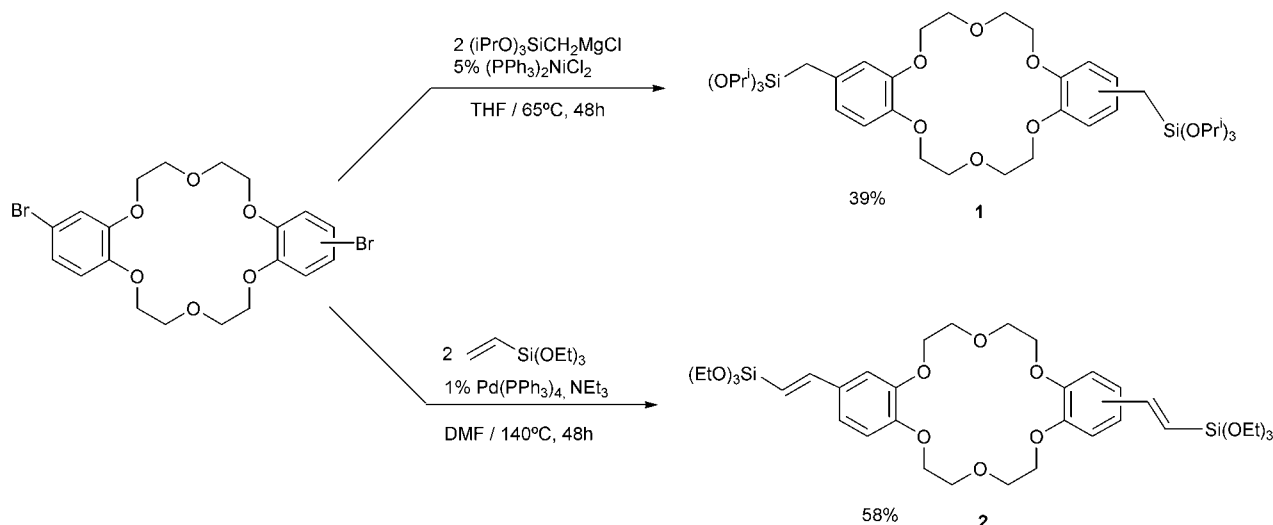
Scheme 1

sensitive product from hexane extraction by using a Soxhlet (Scheme 2).

Complexation of K$^+$ ions by the silylated macrocycles **1**, **2** and **3** was performed in the presence of 1 equivalent of KSCN in EtOH heated under reflux for 5 minutes to give quantitatively the corresponding 1:1 **1–3[K$^+$]** complexes. Treatment of **1** with 1 equivalent of NaSCN under the same conditions gave quantitatively the corresponding 1:1 **1[Na$^+$]** complex. The formation of the complexes was first indicated by a change of solubility. While the compounds **1**, **2** and **3** are rather soluble at room temperature in pentane and hexane, the complexes are not. All these complexes were characterised by their ^{1}H NMR spectra which displayed only one signal for the methylene protons, except for **3[K$^+$]**, while the ^{1}H NMR spectra of the starting macrocycles showed 2 signals for the same protons (Table 1). The complexation of K$^+$ cations by the silylated macrocycles **1**, **2** and **3** as well as that of Na$^+$ by **1** was confirmed by diffuse reflectance IR spectroscopy (DRIFTS). Indeed, the DRIFT spectra of complexed salts exhibited only one absorption band for the C≡N stretching vibration while the DRIFT spectra for KSCN and NaSCN displayed two C≡N stretching vibrations and at lower frequencies (Table 1). It is worth noting that the IR spectra of dibenzo-18-crown-6-KSCN and NaSCN complexes[25] displayed also one C≡N stretching vibration. A further indication for the formation of the complex **1[Na$^+$]** was given from the solid state ^{23}Na NMR spectrum which displays a signal at δ −25.6 while that of NaSCN appears at δ −10.6 under the same conditions. It is also to be noted that the ^{23}Na chemical shift for **1[Na$^+$]** is close to that of dibenzo-18-crown-6-[Na$^+$] complex (δ −26.9).

Sol–gel processing of 1, 2 and 3 and characterisation of the corresponding xerogels

The hydrolysis and polycondensation of precursors **1**, **2** and **3** were performed in THF solutions (1 M in precursor) in the presence of a stoichiometric amount of water. The experimental conditions of gelification (catalyst, temperature) are

reported in Table 2. The gel formation from **1** (compound containing two hydrolysable Si(OiPr)$_3$ groups) was conducted with 10 mol% of HCl as catalyst while those of **2** (two hydrolysable Si(OEt)$_3$ groups) and **3** (four hydrolysable Si(OMe)$_3$ groups) were performed under nucleophilic conditions (1 mol% of tetrabutylammonium fluoride) at different temperatures. Gelification of **2** and **3** took place also in the absence of catalyst (Table 2, entries 2 and 5). In all cases, gelification occurred within 30 min except from **1** for which the gelification appeared after several hours (<12 h) no doubt because of the bulky Si(OiPr)$_3$ groups.[13b] Dried gels obtained after the work up given in the experimental section were described by the following nomenclature: first, an **X** to denote xerogels followed by the number designation of the monomer (**1**, **2** or **3**), and last a letter (**A**, **B** or **C**) for the experimental conditions of the reaction: **A**, without catalyst; **B**, 1% of TBAF at room temperature; **C**, 1% of TBAF at 110 °C in a sealed tube.

The solid state ^{29}Si NMR spectra of the xerogels displayed a set of resonances lying between −59 ppm and −78 ppm assigned to T^1 [C–Si(OR)$_2$OSi], T^2 [C–Si(OR)(OSi)$_2$], and T^3 [C–Si(OSi)$_3$] substructures (Table 2). The ^{29}Si NMR spectra of xerogels **X2(A–C)** are shown as examples in Fig. 1. The absence of resonance corresponding to Q substructures[26] (region of −100 ppm) attested that no cleavage of Si–C bonds occurred during the sol–gel process. The degree of condensation of the hybrid materials, σ, was evaluated by deconvolution of the individual T resonances[27,28] (Table 3). It appears that the higher the temperature of reaction, the greater the degree of condensation (compare in Table 3 entries 3, 4 and entries 6, 7). It is also worth noting that the polycondensation of the monomer **2** is complete in the presence of 1% of TBAF at 110 °C. Elemental analysis showed that all the hybrid materials deviated from the ideal stoichiometry based on totally polycondensed silsesquioxane materials. Except for **X2C** which is a very well condensed material, these analyses revealed an excess of carbon and hydrogen (Table 3) indicating the
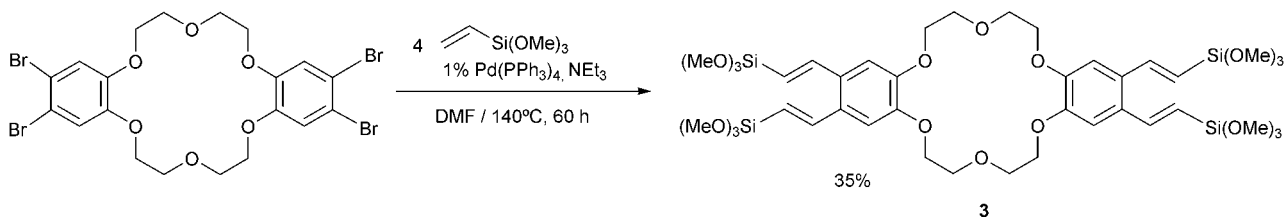

Scheme 2

Table 1 ^{1}H NMR and DRIFT data^a for **1–3[K$^+$]** and **1[Na$^+$]** complexes

	1	1[K$^+$]	1[Na$^+$]	2	2[K$^+$]	3	3[K$^+$]
^{1}H NMR, δ CH$_2$O	3.96, 4.07	4.16	4.11	4.08, 4.20	4.18	4.07, 4.24	4.10, 4.15
DRIFT, ν_{CN}/cm^{-1}		2051	2059		2055		2056

^{a}ν_{CN} (cm^{-1}) for KSCN 2042, 2004; for NaSCN 2073, 2024; for dibenzo-18-C-6–[K$^+$] 2055; for dibenzo-18-C-6–[Na$^+$] 2065.[26]

presence of residual hydroxy or alkoxy groups. The gap between the experimental and the ideal values is higher especially when the degree of condensation of the material is low, as could be expected. Powder X-ray diffraction data for xerogels showed that these materials are amorphous. The surfaces areas determined by adsorption–desorption of N$_2$ (BET)[29] were found to be very low (<10 m^2 g^{-1}) for all the materials, whatever the experimental conditions of the preparation.

Preparation and characterisation of the xerogels X1[K$^+$], X1[Na$^+$], X2[K$^+$] and X3[K$^+$]

Sol–gel polycondensations of complexes **1[K$^+$]**, **1[Na$^+$]**, **2[K$^+$]** and **3[K$^+$]** were performed at room temperature in 0.5 M THF solution with a stoichiometric amount of water. While in the presence of 10 mol% of HCl the gel formation of **1** took almost 12 h, those of **1[K$^+$]** and **1[Na$^+$]** were very fast (<5 min). This large difference in gel times could be attributed most probably to a partial protonation of the free oxygen atoms of the crown ether **1**, thus decreasing the catalytic activity of HCl. Gelation of **2[K$^+$]** was conducted in the presence of 1% TBAF, while that of **3[K$^+$]** took place without any catalyst probably because of the presence of four hydrolysable Si(OMe)$_3$ groups per crown ether instead of two hydrolysable Si(OEt)$_3$ groups for **2[K$^+$]**. Dried gels obtained after the work up given in the experimental section are denoted by an initial **X** to denote xerogel followed by the designation of the complex (Table 4).

The ^{29}Si CP-MAS NMR spectra of the xerogels revealed that there was no cleavage of the Si–C bond during the sol–gel process as was observed for the free monomer and that the condensation was incomplete (Table 4). DRIFT spectra of the xerogels showed that the $\nu_{(C\equiv N)}$ stretching band is very close to that observed for the corresponding starting complexes in all cases (compare $\nu_{(C\equiv N)}$ in Table 1 for the complex and $\nu_{(C\equiv N)}$ in Table 4 for the corresponding xerogel). Another datum was given for **X1[Na$^+$]** from the solid state ^{23}Na NMR spectrum which displays one broad signal centred at δ -26.3 (δ -10.6 for NaSCN under the same conditions) and another signal at δ 0.1 attributed to NaCl. The presence of NaCl in the material was confirmed by powder X-ray diffraction data. Formation of NaCl should be due to a displacement of complexed Na$^+$ ions by the HCl used as catalyst for the gel formation, and should then be limited to almost 10%. The same phenomenon occurs

for **X1[K$^+$]** as the powder X-ray diffraction pattern indicates the presence of KCl.

The N$_2$ BET surface areas of the materials incorporating sodium and potassium salts were found to be very low (<10 m^2 g^{-1}) in all cases. Finally, elemental analysis revealed that during the sol–gel polymerisation about 95% of alkali cations were retained within the xerogel indicating that the polycondensation occurred without distortion of the conformation of the crown ether/salt complex. It is not surprising that the strong interactions between the crown ether and the salt survive the sol–gel process as it has been shown that weak interactions remain unchanged during the sol–gel process.[15(d)]

Cation-binding properties of the xerogels

The binding ability towards sodium or potassium cations of xerogels **X1**, **X2(A–C)** and **X3(A–C)** was investigated. Each solid was treated with 1 equiv. of NaSCN or KSCN in EtOH for 12 h at room temperature or heated under reflux. The selectivity of the xerogels towards Na$^+$ and K$^+$ ions was likewise studied by competition experiments from a 1:1 mixture of NaSCN and KSCN in EtOH. The amount of non-complexed cations was measured by flame spectrophotometry after filtration of the reaction mixture followed by washing of the residue with EtOH until no more salt was recuperated, and then evaporation of the solvent, and dissolution of the recovered alkali metal salt in water. From these data, the cations uptake into the xerogels was inferred and reported in Tables 5, 6 and 7. Further confirmation of the incorporation of salts was given by elemental analyses. It is important to note that the results given by these two methods of titration are in good agreement. From DRIFT spectroscopy, it was proved that the salts are not only incorporated within the hybrid materials but complexed by the crown ether moieties, only one C≡N stretching band being observed (Tables 5, 6 and 7) at wavenumbers very close to those of the corresponding complexes (Table 1). The complexation of the Na$^+$ ions was also shown from the solid state ^{23}Na NMR spectra of xerogels incorporating NaSCN which display in all cases an upfield resonance (δ lying between -19.2 and -26.6) (Tables 5, 6, and 7) with respect to the signal of NaSCN (δ -10.6) under the same conditions, the resonances being close to that observed for the complex **1[Na$^+$]** (δ -25.6).

The survey of cations uptake into **X1** (Table 5) at room temperature shows that:
(1) 72% (entry 2a) of crown ether moieties are able to

Table 2 Hydrolysis and polycondensation of precursors **1–3** (1 M in THF) in the presence of a stoichiometric amount of water. ^{29}Si CP-MAS NMR data of the xerogels

Entry	Monomer	Catalyst	T/°C	Xerogel	^{29}Si CP-MAS NMR (δ)^a		
					T^1	T^2	T^3
1	**1**	HCl 10%	22	**X1**	-55	**-62**	-70
2	**2**	—	0	**X2A**^{b}	-59	**-69**	-76
3	**2**	TBAF 1%	22	**X2B**	-59	-70	**-76**
4	**2**	TBAF 1%	110^c	**X2C**			**-76**
5	**3**	—	24	**X3A**	**-61**	-70	
6	**3**	TBAF 1%	24	**X3B**	-62	**-70**	-78
7	**3**	TBAF 1%	110^c	**X3C**^{d}	-61	**-70**	-78

^{a}Major resonances in bold. ^{b}0.5 M THF solution of **2**. ^{c}Sealed tube. ^{d}0.5 M THF solution of **3**.
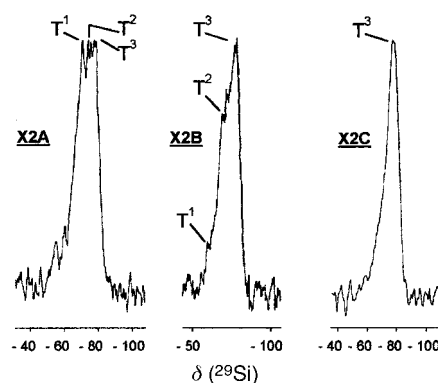

Fig. 1 ^{29}Si CP-MAS NMR spectra of xerogels **X2A**, **X2B**, and **X2C**.

Table 3 Results of deconvolution analysis of the ^{29}Si CP-MAS NMR spectra of xerogels and their elemental analyses

Entry	Xerogel	Degree of condensation σ (%)	Elemental analysis Ideal formula	Experimental formula
			Ideal formula	Experimental formula
1	**X1**	71	$C_{22}H_{26}Si_2O_9$	$C_{24.3}H_{31.6}Si_2O_{10.3}$
2	**X2A**	77	$C_{24}H_{26}Si_2O_9$	$C_{26.6}H_{31.6}Si_2O_{11.6}$
3	**X2B**	81	$C_{24}H_{26}Si_2O_9$	$C_{25.9}H_{30.2}Si_2O_{10.2}$
4	**X2C**	99	$C_{24}H_{26}Si_2O_9$	$C_{23.7}H_{26.4}Si_2O_{9.8}$
5	**X3A**	48	$C_{28}H_{28}Si_4O_9$	$C_{33.8}H_{44.8}Si_4O_{16}$
6	**X3B**	63	$C_{28}H_{28}Si_4O_9$	$C_{32}H_{42}Si_4O_{15.2}$
7	**X3C**	72	$C_{28}H_{28}Si_4O_9$	$C_{32}H_{39.7}Si_4O_{15.8}$

complex K^+ ions

(2) 47% (entry 1a) of crown ether moieties are able to complex Na^+ ions

These results are very different from those observed in solution as in ethanol, the complexation of K^+ ions on one hand, and that of Na^+ ions on the other hand by the precursor **1** take place quantitatively to yield **1[K$^+$]** and **1[Na$^+$]** complexes.

Furthermore, about 12% of the crown ether moieties are able to complex Na^+ in the presence of K^+ (entry 3a). As about 47% of the crown ether moieties are able to complex Na^+ ions in the absence of K^+ ions (entry 1a), we can conclude that about 35% of the complexing sites are able to complex both ions but preferentially K^+ ions. 78% of crown ethers being able to complex K^+ ions in the presence of Na^+ ions at room temperature (entry 3a), we can infer that about 43% (78−35) of the crown ether moieties complex K^+ ions. The results obtained in ethanol heated under reflux are very similar (Table 5, entries 1b, 2b, 3b). Thus, overall the results reported in Table 5 suggest that within the material **X1** crown ether moieties exist with different binding properties:

(1) the **A** sites are able to complex both ions but preferentially K^+ ions (about 35%)

(2) the **B** sites complex K^+ ions but not Na^+ ions (about 43%)

(3) the **C** sites complex Na^+ ions (about 12%) but not K^+ ions

(4) A fourth kind of binding site exits, *i.e.*, the D sites, which are not accessible for salts in EtOH or unable to chelate Na^+ or K^+ ions (about 10%).

An examination of the results reported in Tables 6 and 7 leads also to the evidence that these four types of chelating site exist also in xerogels **X2(A–C)** and **X3(A–C)**. An estimation of the percentage of each type of site in a given xerogel is outlined in Table 8.

Further observations emerge from Table 8:

(1) the percentage of each type of chelating site depends on the nature of the xerogels

(2) the A sites are notably more important in the xerogel **X1** than in the others

(3) the percentage of **A** sites increases within a family of xerogels [**X2(A–B)** or **X3(A–C)**] with the degree of condensation σ of the xerogels (reported in Table 3), producing as a consequence a concomitant decrease of **B** and/or **C** sites

(4) the percentage of **B** sites is always notably superior to the percentage of **C** sites for a given xerogel

(5) the percentage of **D** sites seems mainly to depend on the nature of the precursor

Discussion

To explain these experimental results we propose the following interpretation.

The existence of the different types of chelating sites could be due to the more or less important deformation undergone by the crown ether moieties during the sol–gel process. One of the causes for the deformations could very likely originate from the existence of hydrogen bonds between the SiOH groups and the oxygen atoms of the crown ethers and thus should be related to the degree of condensation of the network.

The **A** sites which are able to complex both ions should be relatively more flexible than the **B** and **C** sites. The latter should be deformed in such a way that one type (**B** sites) complexes K^+ ions and the other (**C** sites) complexes Na^+ ions.

It can be noted that going from **X2A** to **X2C** or from **X3A** to **X3C**, there is in both cases an increase in the percentage of **A** sites, the increase being notably more important in the latter case. As going from **X2A** to **X2C** and from **X3A** to **X3C** there is an increase in the degree of condensation of the xerogels (Table 3) with a concomitant decrease of the SiOH groups able to bind the oxygen atoms of the crown ether, this confirms that there is a relation between the percentage of **A** sites and the degree of condensation of the network. The greater the degree of condensation σ, the higher the percentage of **A** sites. The hydrogen bonding should reduce the mobility of the crown ether and as a consequence the possibility to change conformation for the complexation of Na^+ or K^+ ions. The greater increase in **A** sites in the series **X3(A–C)** in comparison with the series **X2(A–C)** agrees with this interpretation as for a given degree of condensation σ the number of SiOH groups in the xerogels **X3(A–C)** is more important than in the xerogels **X2(A–C)** (the precursor **3** containing four hydrolysable $Si(OR)_3$ groups while the precursor **2** contains only two).

However, this explanation is not sufficient to explain the high percentage of **A** sites within **X1**, since, while the degrees of condensation of **X1** and of **X2A** are rather similar (Table 3), the percentage of **A** sites within **X1** (35%) is clearly more important than that within **X2A** (7%). We consider that the high ratio of **A** sites in **X1** is due to the nature of the methylene spacer which is

Table 4 Hydrolysis and polycondensation of complexes. Spectroscopic data of the xerogels

Monomer	Catalyst	$T/°C$	Xerogel	^{29}Si CP-MAS NMR data^a			DRIFT ν_{CN}/cm^{-1}
				T^1	T^2	T^3	
1[K$^+$]	HCl 10%	24	**X1[K$^+$]**	−53	**−61.6**	−68	2056
1[Na$^+$]	HCl 10%	22	**X1[Na$^+$]**		**−62.6**		2060
2[K$^+$]	TBAF 1%	19	**X2[K$^+$]**		−70	**−79**	2057
3[K$^+$]	—	20	**X3[K$^+$]**	−61	**−69**	−78	2057

^{a}Major resonances in bold.

Table 5 Yield (%) of alkali metal cations incorporated within the xerogel **X1** and spectroscopic data of the xerogel after reaction

Entry	Salt	$T/°C$	% Na$^+$	% K$^+$	DRIFT ν_{CN}/cm^{-1}	^{23}Na NMR δ
1a	NaSCN	20	47,^{a} 47^b		2068	−24.2
1b		78	43,^{a} 46^b		2063	−23.4
2a	KSCN	20		72,^{a} 73^b	2059	
2b		78		77,^{a} 76^b	2055	
3a	NaSCN–KSCN (1:1)^c	20	12^a	78,^{a} 78^b	2054	−22
3b	NaSCN–KSCN (1:1)^c	78	10^a	74,^{a} 76^b	2054	−19.2

^{a}Measured by elemental analyses. ^{b}Measured by flame spectrophotometry. ^{c}Competitive experiments.

more flexible than the ethenyl group bound to silicon in the precursors **2** and **3**. As the **A** sites involve a greater flexibility than the other sites, this factor can explain the high ratio of **A** sites in **X1**. Previous studies have shown the importance of greater or lesser flexibility of the organic spacer in the properties of hybrid materials.[28]

The changes in the percentage of **D** sites with the nature of the xerogel [about 10% for the xerogel **X1**, about 23% for the xerogels **X2(A–C)** and about 43% for **X3(A–C)** (Table 8)] are also of interest. First, it is worth noting that the lowest percentage of **D** sites is observed within **X1** which presents the highest percentage of **A** sites, and the highest percentage of **D** sites (48%) is within **X3A**, which presents the lowest percentage of **A** sites (0%). Furthermore, as there are 23% of **D** sites in the xerogel **X2C**, a very well condensed solid ($\sigma = 99\%$), the existence of the **D** sites cannot be explained by hydrogen bonding between the oxygen atoms of the crown ether. We consider that the percentage of **D** sites in a given xerogel directly depends on the monomer which is essentially characterised by the nature of the spacer (flexible for **1**, rigid for **2** and **3**) and by the number of hydrolysable Si(OR)$_3$ groups (two for **1** and **2** and four for **3**). Thus, as the degrees of condensation of **X1** ($\sigma = 71\%$) and of **X2A** ($\sigma = 77\%$) are in the same range, the low percentage of **D** sites (10%) within **X1** in comparison with **X2A** (23%) should be due to the flexible methylene spacers of the monomer **1**. The high percentage of **D** sites within **X3(A–C)** should be essentially due to the presence of four hydrolysable groups in the monomer **3**. This gives rise to a large number of remaining SiOH bonds in the xerogel and as a consequence to a low flexibility of the organic moiety due to the four SiO$_{1.5}$ groups per chelating site. The case of xerogels **X2(A–C)** is in between as they originate from the monomer **2** which presents a rigid spacer and contains only two hydrolysable Si(OR)$_3$ groups.

Conclusion

We have shown that the xerogels prepared from the monomers **1**, **2** and **3** gave rise to non-porous xerogels whatever the experimental conditions of hydrolysis. It was observed that the two routes of incorporation of salts, *i.e.* complexation of the monomers followed by their gelification, or gelification of the monomers followed by the incorporation of salts into these

solids, are not equivalent. Thus, while the gelification of the **3[K$^+$]** complex gives rise to a solid with 95% of its chelating sites containing a K$^+$ cation, the study of the binding ability of xerogels **X3(A–C)** indicates that about 45% of crown ether sites can complex neither K$^+$ nor Na$^+$ ions. This reveals that the gelification takes place with deformation of crown ether moieties. This was confirmed by competitive experiments which have shown that each xerogel displays four types of chelating site, the importance of which depends on the degree of condensation σ of the polysiloxane network, on the flexibility of the spacers between the benzene rings and the silicon centres and on the number of hydrolysable Si(OR)$_3$ groups borne by the precursor. Thus, it appears that the solid alters the general rules of complexation of alkali metal cations with crown ethers. In the solid, the nature of the precursor and the degree of polycondensation of the network become the dominating factors controlling the complexation. They are both conducive to greater or lesser rigidity as well as to greater or lesser deformation of the crown ether moieties in relation to the formation of hydrogen bonds between the remaining SiOH groups and the oxygen atoms of the crown ether.

Experimental

Table 6 Yields (%) of alkali metal cations incorporated within the xerogels **X2A**, **X2B** and **X2C** at room temperature and spectroscopic data of the xerogels after reaction

Entry	Xerogel	Salt	% Na$^+$	% K$^+$	DRIFT ν_{CN}/cm^{-1}	^{23}Na NMR δ
1a	**X2A**	NaSCN	31,^{a} 31^b		2060	−26.5
1b		KSCN		52,^{a} 52^b	2059	
1c		NaSCN–KSCN (1:1)^c	24^a	53,^{a} 52^b	2060	
2a	**X2B**	NaSCN	37,^{a} 34^b		2058	−25.8
2b		KSCN		55,^{a} 49^b	2058	
2c		NaSCN–KSCN (1:1)^c	26^a	55,^{a} 48^b	2058	
3a	**X2C**	NaSCN	33,^{a} 32^b		2058	−22.8
3b		KSCN		56,^{a} 55^b	2058	
3c		NaSCN–KSCN (1:1)^c	18^a	56,^{a} 58^b	2058	

^{a}Measured by elemental analyses. ^{b}Measured by flame spectrophotometry. ^{c}Competitive experiments.

Table 7 Yields (%) of alkali metal cations incorporated into the xerogels **X3A**, **X3B** and **X3C** at room temperature and spectroscopic data of the xerogels after reaction

Entry	Xerogel	Salt	% Na$^+$	% K$^+$	DRIFT ν_{CN}/cm^{-1}	^{23}Na NMR δ
1a	**X3A**	NaSCN	12,^{a} 10^b		2063	−26.6
1b		KSCN		37,^{a} 39^b	2059	
1c		NaSCN–KSCN (1:1)^c	15^a	35,^{a} 38^b	2059	
2a	**X3B**	NaSCN	24,^{a} 19^b		2063	−24.6
2b		KSCN		45,^{a} 45^b	2058	
2c		NaSCN–KSCN (1:1)^c	17^a	44,^{a} 43^b	2059	
3a	**X3C**	NaSCN	35,^{a} 35^b		2063	−23.2
3b		KSCN		48,^{a} 48^b	2060	
3c		NaSCN–KSCN (1:1)^c	13^a	47,^{a} 49^b	2058	

^{a}Measured by elemental analyses. ^{b}Measured by flame spectrophotometry. ^{c}Competitive experiments.

PHF 106 HYCEL apparatus. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS.

4,4′,5,5′-Tetrabromodibenzo-18-crown-6 ether

In a 1000 ml three-necked flask with a mechanical stirrer, an isobar dropping funnel and a reflux condenser connected to a gas absorption trap, 8 g (22 mmol) of dibenzo-18-crown-6 were placed in an acetic acid solution (600 ml). An acetic acid solution of bromide (100 ml, 98 mmol) was then rapidly added. The solution became orange and release of HBr was observed. The reaction mixture was heated under reflux at 95 °C for 12 h. The 4,4′,5,5′-tetrabromodibenzo-18-crown-6 precipitated while discoloration of the solution was progressively observed. When the reaction mixture was at room temperature, the precipitate was filtered off and washed three times with 50 ml of ether to give 12 g (17.7 mmol, 80%) of 4,4′,5,5′-tetrabromodibenzo-18-crown-6 ether as a white powder. Mp 221–223 °C. ^{1}H NMR (δ, 250 MHz, CDCl$_3$) 3.98 (s, 8H, OCH$_2$), 4.09 (s, 8H, OCH$_2$), 7.04 (s, 4H, Ar); ^{13}C NMR (δ, 50 MHz, CDCl$_3$, {H}) 70.1 (CH$_2$), 70.8 (CH$_2$), 116.3 (CH), 118.9 (CH), 149.7 (C). MS (IE, 70 eV): $m/z = 676$ ((M$^+$), 43%). Anal. calc. for C$_{20}$H$_{22}$Br$_4$O$_6$: C, 35.50, H, 2.96, Br, 47.30%. Found: C, 35.75, H, 2.98, Br, 47.04%.

4,4′(5′)-Bis(triisopropoxysilylmethyl)dibenzo-18-crown-6 ether–KSCN complex 1[K$^+$]

520 mg (0.65 mmol) of **1**,^{20} 63 mg (0.65 mmol) of KSCN and 10 ml of dry ethanol were placed in a 50 ml Schlenk tube and heated under reflux for 5 min. The solvent was then removed and the residue was washed twice with 20 ml of pentane to yield 580 mg of **1[K$^+$]** (0.65 mmol, 100%) as a white powder. ^{1}H NMR (δ, 250 MHz, CDCl$_3$) 1.36 (d, 36H, CH$_3$), 2.10 (s, SiCH$_2$, 4H), 4.16–4.19 [m, 22H, (OCH$_2$ and CH)], 6.71–6.78 (m, 6H, Ar); ^{13}C NMR (δ, 50 MHz, CDCl$_3$, {H}) 21.6 (CH$_2$Si), 25.9 (CH$_3$), 65.7 (CH), 67.1, 69.3 (OCH$_2$), 110.8, 112.6, 121.9 (CH, Ar), 131.7, 144.4, 146.6 (C, Ar); ^{29}Si NMR (δ, 40 MHz, CDCl$_3$) −54.9 (s). IR (ν/cm^{-1}, DRIFT, KCl) 2051. MS (FAB+, NBA) 835 [(M+K)$^+$, 40%]; 39 (K$^+$, 100%). Anal. Calc. for C$_{41}$H$_{68}$O$_{12}$Si$_2$KSN: C, 55.08, H, 7.61, S, 3.58%. Found: C, 54.87, H, 7.23, S, 3.84%.

4,4′(5′)-Bis(triisopropoxysilylmethyl)dibenzo-18-crown-6 ether–NaSCN complex 1[Na$^+$]

This complex was obtained in an identical manner to that described above from 0.9 g (0.11 mmol) of **1** yielding a white powder of **1[Na$^+$]** (0.99 g, 0.11 mmol, 100%). Mp 153–154.5 °C. ^{1}H NMR (δ, 250 MHz, CDCl$_3$) 1.14 (d, 36H, CH$_3$), 2.07 (s, 4H, SiCH$_2$), 4.11–4.13 [m, 22H, (OCH$_2$ and CH)], 6.68–6.75 (m, 6H, Ar); ^{13}C NMR (δ, 50 MHz, CDCl$_3$, {H}) 21.6 (CH$_2$Si), 25.9 (CH$_3$), 65.6 (CH), 67.1, 68.9 (OCH$_2$), 110.8, 112.5, 121.7 (CH, Ar), 131.5, 132.9, 144.7, 146.8 (C, Ar); ^{29}Si NMR (δ, 40 MHz, CDCl$_3$) −54.9 (s). CP MAS ^{23}Na NMR (δ, 79.38 MHz): −25.6. IR (ν/cm^{-1} DRIFT, KCl) 2059. MS (FAB+, NBA) 819 [(M+Na)$^+$, 100%]; 23 [(Na$^+$), 42%]. Anal. calc. for C$_{41}$H$_{68}$O$_{12}$Si$_2$NaSN: C, 56.10, H, 7.75, S, 3.65, N, 1.59%. Found: C, 56.09, H, 7.58, S, 3.49, N, 1.62%.

4,4′(5′)-Bis(triethoxysilylethen-2-yl)dibenzo-18-crown-6 ether 2

5 g (9.65 mmol) of dibromodibenzo-18-crown-6 ether, 8.14 ml (38.6 mmol) of vinyltriethoxysilane, 6.7 ml (48.3 mmol) of triethylamine, 0.11 g (9.65 mol) of tetrakis(triphenylphosphine) palladium and 80 ml of freshly distilled DMF were placed in a 150 ml Schlenk tube. The solution was heated under reflux for 48 h under argon. The solvent was then removed under vacuum to give a brown oil which was dissolved in CCl$_4$ (100 ml). After filtration of the solution and concentration of the filtrate, the residue was again taken up in ether (2 × 50 ml) and the solution was again filtered. After removal of the solvent, a foam was obtained which was washed with pentane (2 × 15 ml). This foam was pumped under vacuum for 12 h to give a beige powder. The product was extracted from hot pentane (2 × 50 ml) to give after removal of the solvent 4.2 g (58%) of **2**. Mp 69–71 °C. ^{1}H NMR (δ, 250 MHz, CDCl$_3$): 1.29 (t, 18H, CH$_3$), 3.91 (q, 12H, SiOCH$_2$), 4.08 (m, 8H, OCH$_2$), 4.20 (m, 8H, OCH$_2$), 5.99 (d, $^3J_{H,H} = 20$ Hz, 2H, CH=CH), 6.81–7.04 (m, 6H, Ar), 7.14 (d, $^3J_{H,H} = 20$ Hz, 2H, CH=CH); ^{13}C NMR (δ, 50 MHz, CDCl$_3$, {H}) 18.6 (CH$_3$), 58.9 (SiOCH$_2$), 69.1, 70.2 (OCH$_2$), 111.5, 113.3, 115.5, 121.3, 131.7, 149.0, 149.9 (CH=CH, Ar); ^{29}Si NMR (δ, 40 MHz, CDCl$_3$) −55.9 (s). Anal. calc. for C$_{36}$H$_{56}$O$_{12}$Si$_2$: C, 58.69, H 7.61%. Found: C, 59.10, H, 7.73%.

Table 8 Estimation of the percentage of each type of site in xerogels after complexation of salts at room temperature

Xerogel	A sites^a	B sites^b	C sites^c	Accessible sites	D sites^d
X1	35	43	12	90	10
X2A	7	46	24	77	23
X2B	10	42	26	78	22
X2C	15	42	18	75	25
X3A	0	37	15	52	48
X3B	5	39	17	61	39
X3C	22	26	13	61	39

^{a}Able to complex both ions but preferentially K$^+$. ^{b}Complex K$^+$ ions. ^{c}Complex Na$^+$ ions. ^{d}Sites not accessible for salts or unable to chelate Na$^+$ or K$^+$ ions.

4,4′(5′)-Bis(triethoxysilylethen-2-yl)dibenzo-18-crown-6 ether–KSCN complex 2[K⁺]

This complex was prepared in the same way as **1[K⁺]** starting from 1.1 g (1.5 mmol) of **2** to yield a beige powder (1.25 g, 1.5 mmol, 100%). Mp 115 °C (decomp.). ^{1}H NMR (δ, 250 MHz, CDCl$_3$) 1.28 (t, 18H, CH$_3$), 3.87 (q, 12H, SiOCH$_2$), 4.18 (m, 16H, OCH$_2$), 6.01 (d, $^3J_{H,H} = 20$ Hz, 2H, CH=CH), 6.80–7.07 (m, 6H, Ar), 7.23 (d, $^3J_{H,H} = 24$ Hz, 2H, CH=CH); ^{13}C NMR (δ, 50 MHz, CDCl$_3$, {H}) 18.7 (CH$_3$), 59.0 (SiOCH$_2$), 67.5, 67.7, 69.2 (OCH$_2$), 109.0, 111.3, 116.5, 121.3, 131.9, 147.3, 147.8, 148.6 (CH=CH, Ar); ^{29}Si NMR (δ, 40 MHz, CDCl$_3$) −56.3 (s). IR (v/cm^{-1} DRIFT, KCl) 2055. MS (FAB+, NBA) 775 [(M+K)$^+$, 25%], 39 [(K$^+$), 100%]. Anal. calc. for C$_{37}$H$_{56}$O$_{12}$Si$_2$KSN: C, 53.30, H, 6.72%. Found: C, 53.49, H, 6.83%.

4,4′,5,5′-Tetrakis(trimethoxysilylethen-2-yl)dibenzo-18-crown-6 ether 3

7 g (10.4 mmol) of tetrabromodibenzo-18-crown-6 ether, 12.64 ml (41.4 mmol) of vinyltrimethoxysilane, 15 ml (0.1 mol) of triethylamine, 0.12 g (0.1 mmol) of tetrakis(triphenylphosphine)palladium and 150 ml of freshly distilled DMF were placed in a 500 ml Schlenk tube. The solution was heated under reflux for 60 h under argon. The solvent was then removed under vacuum to give a brown oil. This oil was taken up again in CCl$_4$ (150 ml) and the solution was filtered. After filtration and concentration of the filtrate, the residue was again taken up in ether (2 × 50 ml) and the solution was filtered. After removal of the solvent, a foam was obtained which was pumped under vacuum for 12 h to give a brown powder. The product was extracted for 24 h from hot hexane (200 ml) by using a soxhlet. After removal of the solvent 3.3 g (3.5 mmol, 34%) of **3** were obtained. Mp 70–72 °C. ^{1}H NMR (δ, 250 MHz, CDCl$_3$) 3.65 (s, 36H, CH$_3$), 4.07 (m, 8H, OCH$_2$), 4.24 (m, 8H, OCH$_2$), 5.88 (d, $^3J_{H,H} = 19$ Hz, 4H, CH=CH), 6.94 (s, 4H, Ar), 7.46 (d, $^3J_{H,H} = 19$ Hz, 4H, CH=CH); ^{13}C NMR (δ, 50 MHz, CDCl$_3$, {H}) 51.0 (CH$_3$), 68.4, 70.3 (OCH$_2$), 111.1 (CH, Ar), 117.9 (CH=CH), 130.4 (C, Ar), 146.9 (CH=CH); 149.8 (C, Ar). ^{29}Si NMR (δ, 40 MHz, CDCl$_3$) −53.6 (s). Anal. calc. for C$_{40}$H$_{64}$O$_{18}$Si$_4$: C, 50.85, H, 6.78%. Found: C, 51.95, H, 6.96%.

4,4′,5,5′-Tetrakis(trimethoxysilylethen-2-yl)dibenzo-18-crown-6 ether–KSCN complex 3[K⁺]

This complex was prepared in the same way as **1[K⁺]** starting from 1.41 g (1.5 mmol) of **3** to give a beige powder (1.55 g, 1.49 mmol, 99%) of **3[K⁺]**. ^{1}H NMR (δ, 400 MHz, CDCl$_3$) 3.57 (s, 36H, CH$_3$), 4.10 (m, 8H, OCH$_2$), 4.15 (m, 8H, OCH$_2$), 5.85 (d, $^3J_{H,H} = 19$ Hz, 4H, CH=CH), 6.88 (s, Ar, 4H), 7.45 (d, $^3J_{H,H} = 19$ Hz, 4H, CH=CH). ^{13}C NMR (δ, 100 MHz, CDCl$_3$, {H}) 49.6 (CH$_3$), 66.3, 67.7 (OCH$_2$), 107.5 (CH, Ar), 117.5 (CH=CH), 129.0 (C, Ar), 145.1 (CH=CH), 146.3 (C, Ar). ^{29}Si NMR (δ, 40 MHz, CDCl$_3$) −54.1 (s). IR (v/cm^{-1} DRIFT, KCl) 2056. MS (FAB+, NBA) 983 [(M+K)$^+$, 20], 39 [(K$^+$), 100]. MS (FAB−, NBA) 58 [(SCN)$^-$, 100%]. Anal. calc. for C$_{41}$H$_{64}$O$_{18}$Si$_4$KSN: C, 47.26, H, 6.15, S, 3.07, N, 1.34%. Found: C, 48.51, H, 5.90, S 4.82, N, 0.98%.

Sol–gel processing.

General procedure for the preparation of xerogels X1, X2(A–C), X3(A–C). All the gelifications were carried out from a THF solution of the monomer. A stoichiometric amount of water was first added followed by the required amount of the catalyst. The procedure for the xerogel **X2A** is given as an example. To a THF solution (8.14 ml) of **2** (3 g) placed in a 31 ml flask were added 0.22 ml of water followed by 0.4 ml of a 0.1 M THF solution of TBAF. The flask was cooled at 0 °C and maintained at this temperature until gel formation (<30 mm). After ageing

for 5 days at room temperature, the solid was collected, and washed with ethanol and ether three times. It was powdered after each washing. The solid was dried under vacuum for 2 h at 120 °C yielding 1.84 g of a white powder. The experimental conditions, the gel times and the ^{29}Si NMR data of the xerogels are reported in Table 2 and the elemental analyses in Table 3.

Preparation of xerogels X1[K⁺], X1[Na⁺], X2[K⁺] and X3[K⁺]. The xerogels **X1[K⁺]**, **X1[Na⁺]**, **X2[K⁺]** and **X3[K⁺]** were prepared according to the same procedure. The IR and CP MAS ^{29}Si NMR data are indicated in Table 4.

Complexation of K⁺ and Na⁺ by the xerogels. In all cases, a given xerogel was stirred with an EtOH solution of NaSCN, or of KSCN or of both of them at room temperature or at reflux for 12 h. The quantity of salts introduced into the xerogel was calculated for a completely condensed material. After 12 h of reaction, the mixture was treated according to the following procedure which is given as an example. The IR and CP MAS ^{23}Na NMR data for xerogels **X1** after treatment are indicated in Table 5. The corresponding data for **X2(A–C)** are in Table 6 and for **X3(A–C)** in Table 7.

Complexation of Na⁺ by the xerogel X1. 61 mg of the xerogel **X1**, 9.9 ml of an EtOH solution of NaSCN (solution 1.26×10^{-2} M) and 10.1 ml of EtOH were placed in a flask. The mixture was stirred at room temperature for 12 h and was then filtered. The solid was washed four times with 10 ml of EtOH. It was then dried at 120 °C for 12 h under 20 mmHg to give 57 mg of a white powder.

^{29}Si NMR (δ) −61, −70. ^{23}Na NMR (δ) −24.2. IR (v/cm^{-1} DRIFT, KCl) 2068. Anal. calc. for C$_{23}$H$_{26}$Si$_2$O$_9$NaSN: C, 48.33, Na, 4.03, Si, 9.81%. Found: C, 50.89, Na, 1.90, Si, 9.85%.

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